

***United States Court of Appeals
for the
District of Columbia Circuit***



**TRANSCRIPT OF
RECORD**

JOINT APPENDIX

IN THE
United States Court of Appeals

FOR THE DISTRICT OF COLUMBIA CIRCUIT

—
No. 10,928
—

VANADIUM CORPORATION OF AMERICA, *Appellant,*

v.

JOHN A. MARZALL, COMMISSIONER OF PATENTS,
Appellee.

—
Appeal from the United States District Court for the
District of Columbia.

*United States Court of Appeals
for the
District of Columbia Circuit*

FILED MAR 26 1951

Joseph W. Stewart

CLERK

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Appellee.

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JOINT APPENDIX.

I.

**PLEADINGS, DOCKET ENTRIES AND
OTHER PAPERS.**

122

Filed Sep 25 1948

In the District Court of the United States
For the District of Columbia

Civil Action No. 3977-48

VANADIUM CORPORATION OF AMERICA, 420 Lexington Ave.,
New York, N. Y., *Plaintiff*

v.

LAWRENCE C. KINGSLAND, Commissioner of Patents,
Washington, D. C., *Defendant*

Complaint.

LETTERS PATENT

To the Honorable, the Justices of the District Court of the
United States for the District of Columbia:

Vanadium Corporation of America, plaintiff in the above
entitled action, alleges:

1. Plaintiff, Vanadium Corporation of America, is a corporation duly organized and existing under the laws of the State of Delaware and having a principal place of business at New York City, State of New York.

2. The defendant, Lawrence C. Kingsland, is Commissioner of Patents and has his official residence in the District of Columbia within the jurisdiction of this Court.

3. This is a suit arising under the patent laws of the United States and is based upon the provisions of Section 4915 of the Revised Statutes of the United States as amended by Acts of March 2, 1927, C. 273, Section 11, 44 Stat. 1336, March 2, 1929, C. 488, Section 2(b), 45 Stat. 1476, and August 5, 1939, C. 451, Section 4, 53 Stat. 1212 (U. S. Code, Title 35, Section 63); and is based upon

123 the refusal of the Commissioner of Patents to grant
Letters Patent to the plaintiff upon an application

for Letters Patent hereinafter identified, and of which plaintiff is the sole owner of the entire right, title and interest, except for the license to the United States Government referred to in paragraph 5 hereof.

4. On the 10th day of February, 1942, Frank W. Woodman and Miles B. Royer, being, as the plaintiff is informed and believes and therefore alleges, the original, first and joint inventors of certain new and useful improvements in "Purification of Manganese Salt Solutions," not abandoned, not known or used by others in this country before their invention or discovery thereof, not patented or described in any printed publication in this or any foreign country before their invention or discovery thereof, or more than one year prior to their application hereinafter mentioned, not in public use or on sale in this country for more than one year prior to the date of said application, and not patented nor caused to be patented by themselves or their legal representatives or assigns in any foreign country on an application filed more than twelve months prior to their said application in this country, duly filed in the United States Patent Office an application for Letters Patent for said invention, which application bears Serial No. 430,258.

124 5. The plaintiff owns the complete right, title and interest in and to said application Serial No. 430,258 and to each and every invention therein disclosed, by reason of the conveyance from Frank W. Woodman and Miles B. Royer to the Vanadium Corporation of America, dated April 29, 1946, and recorded on May 21, 1946 in Liber F-207, page 428, Transfers of Patents of United States Patent Office, except that the inventions described in said application may be manufactured and used by or for the United States Government for governmental purposes without the payment of any royalty thereon, in accordance with an agreement between said inventors and plaintiff dated July 25, 1946 and recorded August 2, 1946 in Liber F-208, page 8, Transfers of Patents of the United States Patent Office.

6. The Board of Appeals of the United States Patent Office in a decision rendered on the 26th day of March, 1948, wrongfully refused to allow claims numbered 22, 26, 27 and

28 of said application Serial No. 430,258, as will more fully appear from the record of the application now in the Patent Office, which record or a certified copy thereof plaintiff will produce at the hearing of this case. Said claims are as follows:

Claim 22. A process for producing a purified manganese salt solution amenable to electrodeposition of the manganese content thereof, which comprises subjecting a manganese salt solution to a preliminary purification treatment which removes substantially all iron and heavy metal impurities, said preliminary purification treatment including treatment with a soluble sulfide, thereafter treating said purified solution maintained at a pH of at least 4.5 with a soluble compound of a metal selected from the group
125 consisting of iron, aluminum, beryllium and titanium which precipitates as a hydrate, said soluble compound being used in amount to give about 0.1 gram per liter to 1.0 gram per liter of metal of said group, and recovering a purified solution from the treatment mixture.

Claim 26. A process for producing a purified manganese sulfate solution amenable to electrodeposition of the manganese content thereof, which comprises subjecting a manganese sulfate solution to a preliminary purification treatment which removes substantially all iron and heavy metal impurities, said preliminary purification treatment including treatment with a soluble sulfide, thereafter treating said purified solution maintained at a pH between 7 and 8 with a soluble compound of a metal selected from the group consisting of iron, aluminum, beryllium and titanium which precipitates as a hydrate, said soluble compound being used in amount to give about 0.1 gram per liter to 1.0 gram per liter of metal of said group, and recovering a purified solution from the treatment mixture.

Claim 27. A process for producing a purified manganese sulfate solution amenable to electrodeposition of the manganese content thereof, which comprises subjecting a manganese sulfate solution to a preliminary purification treatment which removes substantially all iron and heavy metal impurities, said preliminary purification treatment includ-

ing treatment with a soluble sulfide, thereafter treating said purified solution maintained at a pH between 7 and 8 with a soluble sulfate of iron which precipitates as a hydrate, said soluble sulfate of iron being used in amount to give about 0.1 gram per liter to 1.0 gram per liter of iron, and recovering a purified solution from the treatment mixture.

Claim 28. A process for producing a purified manganese sulfate solution amenable to electrodeposition of the manganese content thereof, which comprises subjecting a manganese sulfate solution to a preliminary purification treatment which removes substantially all iron and heavy metal impurities so that the solution contains not over about 0.0001 gram per liter of iron, said preliminary purification treatment including treatment with a soluble sulphide, thereafter treating said purified solution maintained at a pH between 7 and 8 with a soluble compound of a metal selected from the group consisting of iron, aluminum, beryllium and titanium which precipitates as a hydrate, said soluble compound being used in amount to give about 0.1 gram per liter to 1.0 gram per liter of metal of said group, and recovering a purified solution from the treatment mixture.

126 7. No appeal has been filed in the United States

Court of Customs and Patent Appeals from any action of the Patent Office in said application, and no appeal is now pending in said Court.

WHEREFORE, plaintiff prays for an order finding that plaintiff is entitled according to law to receive a patent for the said inventions as set forth in the claims specified in Paragraph 6 and for such other and further relief as the Court may deem proper.

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* * * * *

Filed Oct 7 1948

Answer to the Complaint.

To the Honorable, the Judges of the United States District Court for the District of Columbia.

1, 2, 3. Defendant admits the allegations of paragraphs 1, 2 and 3.

4. He admits that on February 10, 1942, Frank W. Woodman and Miles B. Royer, claiming to be the original, first and joint inventors of certain alleged improvements in the "Purification of Manganese Salt Solutions", filed in the Patent Office an application for patent thereon, to which application Serial No. 430,258 was given, and in said application made averments corresponding to the allegations of paragraph 4. He denies, for reasons hereinafter given, that said allegations are sufficient to justify the issuance of a patent on said application.

5. He admits the allegations of paragraph 5.

6. He admits the allegations of paragraph 6 except 130 the allegation that the decision of the Board of Appeals affirming the rejection of claims 22, 26, 27 and 28, of said application, was wrongful. This allegation he denies. He states that the said claims are unpatentable in view of the following prior patents and publications and for the reasons given by the examiner in his statements dated November 5, 1947, and February 16, 1948, and in the decisions rendered by the Board of Appeals on March 26, 1948, and September 28, 1948, copies of which will be furnished at the trial:

Jacobson, 1,137,005, April 27, 1915,

Hannay et al., 2,259,418, Oct. 14, 1941,

Bureau of Mines Report of Investigations, No. 3406, pages 6, 7 and 8,

Prescott and Johnson, Qualitative Chemical Analysis, 5th Edition, pages 114 and 115. Published by D. Van Nostrand Co., N. Y., (1901).

Profert of copies of these patents and publications is hereby made.

7. He admits the allegations of paragraph 7.

W. W. COCHRAN,
Solicitor, U. S. Patent Office,
Attorney for Defendant.

October 6, 1948.

* * * * *

II.

EXCERPTS FROM TESTIMONY AND PROCEEDINGS.

19 Frank William Woodman

was called as a witness by the plaintiff and, being first duly sworn, was examined and testified as follows:

Direct Examination

By Mr. Webb:

* * * * *

20 Q. By whom are you employed at the present time?

A. Southern Alkali Corporation.

Q. Now, will you please state your advanced education?

A. I attended the South Dakota School of Mines from 1924 to 1926. At that time, I went with the Anaconda Copper Mining Company in Great Falls, Montana. In 1928, the Anaconda Company transferred me to Anaconda, Montana, in their new electrolytic zinc plant. I worked in that plant until 1932 as a foreman in the operations.

I attended the South Dakota School of Mines from 1932 to 1934 and graduated in June of 1934.

Q. Following your graduation, what did you do, Mr. Woodman? A. From June until January, I worked with the Empire Mines as a research metallurgist in the amalgamation of gold and the flotation of gold sand and issue of gold, and in January of 1935, I again went back with the Anaconda, Montana, and I was employed by the Anaconda Company in their research department.

In the research department, I worked on various problems for the company, including electrolytic zinc work, vanadium work, arsenic and electrolytic manganese, and several others.

Q. How long did you remain with Anaconda on
21 that occasion, Mr. Woodman? A. I left the Anaconda Company in December of 1940.

Q. What did you do after that? A. I went with the United States Bureau of Mines at Boulder City, Nevada, in December of 1940, and stayed with them until December of 1941.

Q. What was the nature of the job that you had with the Bureau of Mines during that period, what did you do? A. The nature of my work with the Bureau of Mines was research investigation, design of construction, and the installation of a pilot plant at the Boulder City station.

Q. What was that pilot plant for? A. That pilot plant was designed for the purpose of demonstrating to industry the feasibility of electrolytic manganese production.

Q. Now, was that a matter which the Bureau of Mines had previously done experimental work on? A. Yes, the Bureau of Mines had been working on electrolytic manganese from about 1936.

Q. I believe you said you left the Bureau of Mines in December, 1941. Where did you go after that and what did you do? A. I went with Basic Magnesium, Incorporated, at Henderson, Nevada, and for the first six months, the Government sent me to England where I studied the production of magnesium.

22 On return to this country, I was given the position of superintendent of the electrolytic magnesium plant at Basic Magnesium. I held that position for about one year and a half, sufficient to get all of the magnesium cells in operation. Then I was transferred as superintendent of the chlorine and caustic plant at Basic Magnesium.

Q. And how long did you remain with Basic Magnesium?
A. I left Basic Magnesium when the plant shut down about March, 1945.

Q. What did you do after that? A. I was with the Athletic Mining and Smelting Company in Fort Smith, Arkansas, for about one year and a half, that is a retort zinc smelter.

Q. By whom are you employed now? A. The Southern Alkali Corporation.

Q. What is the nature of your job with the Southern Alkali Corporation? A. I am superintendent of engineering in charge of laboratory research work, mechanical, electrical, and all phases of engineering.

Q. What is the nature of the business of the Southern Alkali Corporation, in a general way? A. We manufacture chlorine, caustic, soda ash, hydrogen.

Q. Is that a fairly large producer of caustic, soda
23 ash and so forth?

A. Southern Alkali, along with its affiliate, Columbia Chemicals, are the largest merchant producers of electrolytic chlorine and caustic in the world.

Q. You referred to the various work you have done for the Bureau of Mines, Basic, and Southern Alkali Corporation. Has practically all of that work been of an electro-chemical nature? A. Yes, my work has consisted mainly of electro-chemical procedures.

Q. And are you a member of the Electro-Chemical Society? A. I am.

Q. Now, are you the Frank W. Woodman who, on February 10, 1942, jointly with Miles Royer, filed application, Serial No. 430,258, in the United States Patent Office? A. I am.

Mr. Webb: May I offer in evidence as Plaintiff's Exhibit No. 1, the certified copy of the File Wrapper and Contents, in the matter of the Woodman and Royer application?

The Court: It will be admitted.

(Plaintiff's Exhibit No. 1, File Wrapper and Contents in Woodman and Royer Application, was received in evidence.)

By Mr. Webb:

24 Q. I note the title of your application is "Improvement in Purification of Manganese Salt Solutions." Before discussing the details of your process, I wish you to state to the Court just what manganese is and what the source of it is. A. Well, manganese is a metal. Its main use is in the alloy of steels. There are other uses, but that is the main use today.

The sources of manganese at the present time are, for the United States, Russia, Cuba, Brazil, Africa, those are the main sources of our manganese supply.

Q. There are some manganese ores in this country, are there? A. There are manganese ores in the United States, but they are of insufficient grade or small deposits; they are not commercial deposits, with only one exception that I know of today, and that is at Butte, Montana.

The Court: That is what, you said one exception?

The Witness: One exception today that I am sure the plant is in operation, is at Butte, Montana. That is the only commercial operation I know of today of a large scale.

By Mr. Webb:

Q. How is the manganese recovered from the ore in that operation? A. In the operation now at Butte?

25 Yes, the one you spoke of. A. The ore is mined in Butte and it is brought by railroad to Anaconda. It is ground very fine and flotation is used to upgrade the ore to a higher percentage of manganese. This higher percentage of manganese ore then is run through a big kiln and nodulized, in that form it is shippable then to the steel industry.

Q. I just wanted to bring out that that was not an electrolytic process, is that right? A. That is right, that is not electrolytic.

Mr. Webb: Will you mark that for identification, please, Plaintiff's Exhibit No. 2?

(Plaintiff's Exhibit No. 2, Flow Diagram, Serial No. 430,258, was marked for Identification.)

By Mr. Webb:

Q. Mr. Woodman, I show you a chart which has been marked Plaintiff's Exhibit No. 2. Will you tell us what that chart is, please? A. This is the chart that I prepared in order to show the various steps in the electrolytic manganese procedure.

The Court: This corresponds to this large board that you showed me, doesn't it?

Mr. Webb: Yes, Your Honor, that corresponds to the large chart which I would like to have marked as
26 Plaintiff's Exhibit No. 3.

The Court: Very well.

(Plaintiff's Exhibit No. 3, enlargement of Plaintiff's Exhibit No. 2, was marked for identification.)

Mr. Webb: I offer as Plaintiff's Exhibits Nos. 2 and 3, the charts which have been so marked.

Mr. Cochran: Is this No. 3?

Mr. Webb: No, Mr. Cochran, No. 3 is the enlarged chart of Exhibit No. 2.

Mr. Cochran: No objection.

The Court: They will be received.

(Plaintiff's Exhibits Nos. 2 and 3 were received in evidence.)

By Mr. Webb:

Q. Now, Mr. Woodman, will you please refer to Plaintiff's Exhibit No. 2 and explain to the Court the various steps of your process? In other words, describe the process in detail as shown on the chart and as described in your application. A. The manganese ore as mined is not suitable for the leaching operation with sulphuric acid. Therefore, it is given what is called a reducing roast, in other words, it is thrown into a hot furnace and oxygen is taken away from it. In that form, then, it is fed to
27 Step (2), where it is contacted with sulphuric acid.

The sulphuric acid will leach from the ore the manganese, causing a manganous sulphate solution. The sul-

phuric acid will also leach from the ore impurities in the ore such as iron, arsenic, copper, and nickel. Therefore, the leach solution contains manganese sulphate, ammonium sulphate, and the impurities such as the sulphates of iron, arsenic, copper, nickel, and so forth.

This leach then is filtered in Item (3).

Q. Before you go to Item (3), will you tell us where the ammonia comes from that is in that leach solution, that is ammonium sulphate? A. Yes. The ammonium sulphate is added to the leach solution originally. It is for a purpose, it is added for the purpose of helping deposition of the metal in the manganese electrolytic cell.

Q. Now, will you go ahead and take up the other steps of the process, please? A. After leaching, the ore is filtered from the solution in Step (3) and the ore residue in Step (4) is discarded as being worthless.

The solution from the filter in Step (3) goes to what is called the iron purification, which is Step (5). Here, iron is added to the solution, providing not enough iron has been leached from the ore to carry down with it all of
28 the arsenic which has been leached from the ore.

Air is added to the solution and this precipitates the iron which carries down with it the arsenic, provided a sufficient amount of iron is present. Additional iron is added if this amount is found to be insufficient. This step does not precipitate the copper or nickel, because the copper or nickel is present in the solution as sulphates.

After this step, the iron precipitate is filtered from the solution in Step (6), and in Step (7) the iron-arsenic impurities are discarded because they are worthless.

The solution from the filter is passed to the hydrogen sulphide purification, (8). The filtrate is treated with hydrogen sulphide to convert the sulphates of copper and nickel to sulphides, some of which precipitates and are filtered off. However, copper and nickel sulphides are somewhat soluble in the solution so that the precipitation of copper and nickel sulphides is not complete and small

amounts of copper and nickel sulphides remain dissolved in the solution. This solution is not suitable for the electrodepositing of manganese on a commercial scale.

The Court: Why is that?

The Witness: Because very, very minute amounts of impurities will remain in the solution, impurities so minute that an analytical laboratory cannot detect them, but the electrolytic cell will do it, and it will spoil the deposit.

The Court: All right.

The Witness: After the sulphide purification, the solution is again filtered and the copper-nickel impurities discarded, because they are worthless.

After this filter, the solution goes to the final purification, which is Step (11). Here, iron as ferrous sulphate, along with air, is added to the solution containing copper and nickel sulphides. Some of the ferrous sulphate will react with the copper sulphide and with the nickel sulphide to form iron-copper and iron-nickel sulphides. Such compounds are less soluble than the copper sulphide and nickel sulphide and therefore precipitate.

Any excess iron added here will be precipitated as an iron hydroxide.

This precipitate is then filtered off in Step (12). The solution from the filter in Step (12) is now ready and is fed to the manganese electrolytic cell, Step (15).

The Court: I will take a five-minute recess.

(A short recess was taken.)

By Mr. Webb:

Q. Now, you referred to the electrolytic cell which is illustrated in Item (15) on Exhibit 2, Mr. Woodman. Is that where the manganese itself is electrodeposited from this solution? A. Yes, this purified solution is sent between two electrodes, one being an anode, one being a cathode; an electric current is caused to pass from the anode to the cathode. The manganese metal is de-

posited on the cathode and, after a suitable length of time, the cathode is removed from the solution, the manganese stripped from this cathode, and the cathode again replaced in the solution for further deposition.

Q. What is the character or general appearance of that solution that is fed into the electrolytic cell, is it a clear solution? A. The solution fed to the cell must be sparkling clear.

Q. Now, awhile ago the Court asked why the solution, after having been treated as indicated at (8) on Plaintiff's Exhibit 2, was not suitable for electrodeposition, and you explained about the impurities that were in there. What is the nature of the solution at that stage of the process?

A. The solution at Step (8) has been purified of some of the impurities. There still remains in solution, not as suspended particles but actually in solution, there still remains some impurities which, if allowed to go to the electrolytic cell, will cause what is known as re-solution of the manganese and the manganese will refused to plate.

Q. At that stage, the solution is clear also, isn't it, despite the fact that it contains these impurities?

A. Yes. The solution from Step (8) goes through Filter (9) and in Filter (9) all suspended matter is removed. Therefore, the only things remaining in the solution are the impurities which are soluble and are in solution and therefore cannot be caught on filter (9).

Q. Now, will you please tell us why it is that the addition of ferrous sulphate in Step (5) as you described it and as is set forth on the chart, does not precipitate out or eliminate the copper or nickel so that those impurities can be removed, whereas at a later time in the process, namely, after the hydrogen sulphide treatment and down there in Step (11) the addition of the ferrous sulphate does serve to precipitate out the nickel, cobalt and copper impurities that are in the solution? A. The iron in Step (5) comes from the ore, or can be added. In any event, it is added to a solution where all of the metals are present as sulphates

and iron addition is at this stage of absolutely no effect on removing nickel-cobalt from the solution, whereas in Step (11) after the sulphide purification, those metals are present there as the sulphides and when they are present as the sulphides, the addition of iron will remove those sulphides from solution.

Q. Then, as I understand it, when these impurities
32 are in the sulphate form as they are up in Step (5), the treatment with ferrous sulphate will not remove them and it is not until after you convert the sulphates to sulphides that a ferrous sulphate treatment will remove those impurities, is that it? A. That is correct.

Q. What would happen if you were to add more iron in the form of ferrous sulphate up there in Step (5) as illustrated on the chart, Exhibit 2? A. The addition of more iron in Step (5) would have absolutely no effect whatsoever on the purification. Only sufficient iron is required to remove the arsenic, any additions above that would have absolutely no effect on the purification of the solution.

The Court: What form of iron is used in Step (5) there?

The Witness: In Step (5), if you want to add iron there, you can add ferrous sulphate, you can add a chloride, in this particular case we are adding ferrous sulphate. It is the same iron that you add there (indicating), ferrous sulphate that you would add any other place, it is in the same form.

By Mr. Webb:

Q. In other words, it isn't the pure iron that is added there, it is iron in the form of a sulphate or a
33 chloride? A. It is iron that you must add which will be soluble in the solution.

Q. Now, you have referred to sulphates of copper and nickel and you have also referred to sulphides of copper and nickel and cobalt. Will you please explain briefly the difference between, as for example a copper sulphate and a copper sulphide? A. In this instance, copper sulphate

is a salt which is very soluble in the manganese solutions. When you add hydrogen sulphide you convert the copper sulphate to a copper sulphide. When converted to a copper sulphide, the copper is not as soluble in the manganese solutions as a copper sulphate. The same is true for cobalt or some of the other metals.

Q. Is there any difference from the standpoint of appearance, for example, between copper sulphate and copper sulphide? A. Copper sulphate is a blue crystalline salt, whereas copper sulphide is usually a grey or a black flocculate looking material.

Q. Now, in your description of the process as you gave it, and also as shown in the Plaintiff's Exhibit 2, reference has been made to this addition of ferrous sulphate, that is the iron is added in the form of ferrous sulphate. Are there any other metal sulphates which can be used in place of the iron sulphate and accomplish your purposes? A. Yes, you can use aluminum, you can use beryllium, and titanium.

Q. And if those metals were to be used, I take it that they would have to be added or used in the form of a salt, that is a salt in sulphate or chloride form? A. Yes, they would have to be added to the solution as a soluble salt, that is a salt which can go in solution readily.

Mr. Webb: I wanted to develop that fact, Your Honor, because you will note that Claim 22 speaks of this treatment with a soluble compound, "of a metal selected from the group consisting of," certain of these metals, so that the case is not limited to the use of an iron salt. These other salts may be used.

By Mr. Webb:

Q. Now, where were you working at the time you and Mr. Royer made the invention covered by the application involved here? A. I was working at the Bureau of Mines station at Boulder City, Nevada.

Q. And I believe you said earlier that you were with the Bureau of Mines at that station from December, 35 1940, to December, 1941? A. That is right.

Q. Now, prior to the time that you went with the Bureau of Mines, I believe you said you were with the Anaconda Copper Mining Company? A. That is right.

Q. While you were with that company, did you do some work on this problem of purification of solutions to be used in the electrolytic deposition of manganese? A. Yes, I worked for approximately fifteen months in the research department of Anaconda, Montana, for the Anaconda Mining Company.

Q. And while with Anaconda, did you have also experience with the electrolytic deposition of zinc and the purification of solutions to be used? A. That is right, as part of my research work, I had experimented with the purification of zinc solutions many times.

Q. Now, at the time you started on the work on electrolytic manganese for Anaconda Copper Mining Company, did you make any special study of any process of making electrolytic manganese? A. Yes, when I was assigned the job of investigating the electrolytic manganese problem, the Anaconda Company sent me to Rolla, Missouri, at the

36 Bureau of Mines Station. I studied there for approximately two weeks under a Mr. Shelton, who had accomplished a great deal of the work, of the original work done by the Bureau of Mines at the station at Reno, Nevada. I spent two weeks studying the ore reduction, leaching, purification, and deposition of manganese with him before I went back with the Anaconda Company to pursue the work there.

Q. Is the Mr. Shelton that you refer to, Mr. S. M. Shelton whose name appears on this Bureau of Mines publication R. I. 3406? A. Yes, that is the Mr. Shelton.

Q. Well, now, after you made this study of that subject with Mr. Shelton, and went back to Anaconda, what did you do in so far as manufacture of electrolytic manganese

is concerned? A. I set up a research laboratory electrolytic manganese plant. We worked at this for about fifteen months before coming to the conclusion that the process was not a commercial operation and the Anaconda Copper Mining Company dropped the investigation.

Q. Dropped while you were still with the company, was it? A. Oh, yes, yes.

Q. Will you describe the process that was used there in this work at Anaconda? A. The process that we
37 used at Anaconda was the process as outlined by Mr. Shelton to me in Rolla, Missouri, and it is the one that is outlined in the Bureau of Mines report of investigations 3406.

Mr. Webb: Will you mark that, please, Plaintiff's Exhibit No. 4?

(Plaintiff's Exhibit No. 4, Bureau of Mines R. I. 3406, was marked for identification.)

By Mr. Webb:

Q. Is the Bureau of Mines publication which you referred to as No. 3406, the one which is marked Plaintiff's Exhibit No. 4? A. Yes, that is correct.

Mr. Webb: I offer this report in evidence as Plaintiff's Exhibit No. 4. That, Your Honor, was one of the references relied upon by the Patent Office. In fact, I can say the principal one.

The Court: It is in this folder and in the record of the Patent Office. Very well. It is more legible than the photostat of it.

(Plaintiff's Exhibit No. 4 was received in evidence.)

By Mr. Webb:

Q. Would you state briefly just what the steps are, the principal steps in the purification of the solution which you utilized at Anaconda and which, as you stated a
38 while ago, resulted in this abandonment of the project? A. The steps utilized in the purification

consisted of, first, oxidizing the iron; this removed the iron and carried down with it the arsenic that was leached from the ore. This solution was then filtered from the iron residue and was treated with xanthates according to the recommended Bureau of Mines procedure in R. I. 3406. After treatment with xanthates, the solution was filtered from the precipitate and was given a little sulphur dioxide and fed directly to the electrolytic cell.

Q. I take it, then, there was no purification step involved there after the xanthate treatment? A. No, there was no purification step involved.

Q. What is xanthate? A. Xanthate is a soluble sulphide.

Q. Was xanthate used in the process at Anaconda for the same purpose as the hydrogen sulphide in your process as described earlier? A. Yes, that is correct.

Q. And I believe you said that the project was abandoned while you were still with the company? A. That is right.

Q. Now, were there any others working with you on this electrolytic manganese project at Anaconda? A. Yes,
39 I had assistants because we conducted the tests around the clock, so there would be no interruption of the plating. I also reported to the research director of the Anaconda Company, Mr. Frick, who was very interested in the electrolytic manganese problems.

Q. Who was Mr. Frick? A. Mr. Frick was the research director for the Anaconda Copper Mining Company at Anaconda.

Q. Did you report to Mr. Frick with any degree of regularity in regard to the results that you were accomplishing? A. I reported to Mr. Frick daily on all phases of the research work.

Q. What experience, if any, did this Mr. Frick you speak of have in this electrochemical field and, more specifically, in so far as electrolytic deposition of zinc, manganese and the like is concerned? A. Mr. Frick was and is considered

an expert in the field of electrodeposition. He was one of the originators of the electrolytic zinc process for the Anaconda Copper Mining Company back oh, around the years of 1916, 1918. He also put plants up in South America and also in Poland for the company.

Q. And these daily reports that you say you made to Mr. Frick, did you tell him the difficulties which you
40 were encountering? A. Mr. Frick was well aware of the difficulties that we were encountering at all times.

Q. And did Mr. Frick make any suggestion to you as to how to overcome the difficulties of failure to adequately and properly plate out the manganese? A. No, he made no worthwhile suggestions.

Q. Did you try various expedients at that time to try to accomplish your purposes? A. Yes, we tried several. We substituted calcium sulphide for xanthates, we substituted beryllium sulphides for xanthates, we tried several things in order to be able to make the manganese plate satisfactorily, but we were never able to do so.

Q. During the course of the work that you did at Anaconda, did it occur to you to utilize a ferrous sulphate or any other metallic salt in the purification of the solution after it had previously been treated with the xanthates, a sulphide? A. It did not.

Q. Did Mr. Frick ever make any such suggestion to you? A. He did not.

* * * * *

41 By Mr. Webb:

Q. I don't know whether you have stated this so far, Mr. Woodman, but over how long a period of time did this work at Anaconda on electrolytic manganese continue? A. Approximately fifteen months.

Q. Was Mr. Frick in charge of that work during all that time? A. Yes, he was in active charge.

Q. Now, you stated that you were with the Bureau of Mines at Boulder City from about December, 1940, to December, 1941, and I would like for you to describe a little more in detail what your duties were during that period and what the nature of the work was that you were doing

while there. A. For the first few weeks, I was busy
42 at the Salt Lake station with the design of the pilot plant which was going to be put into operation at the Boulder City station. I was also in charge of the research and later design and construction of the electrolytic manganese cells at the Boulder City station.

Q. When you went with the Bureau of Mines at Boulder City, what process did they have at that time and what was being used? A. The Bureau of Mines at that time had abandoned the xanthates purification as outlined in their report of investigations 3406, and they had substituted for that the use of hydrogen sulphide. Other than that, the procedure was the same as far as the steps were concerned.

Q. In other words, the process they had at that time was the same as that in R. I. 3406 with the exception that they used hydrogen sulphide instead of xanthates? A. That is correct.

Q. You spoke about the pilot plant which was being put in. What was the size of that pilot plant? A. That plant was designed to produce 2,000 pounds per day of electrolytic manganese.

Q. Who were you working under in connection with this work that you did at the Bureau of Mines in 1940 and 1941?

A. I was working under Dr. Koster, who was supervising engineer at the Boulder City station.

43 Q. Do you know what experience Dr. Koster had had in the electrodeposition of manganese? A. Dr. Koster was one of the originators in the Bureau of Mines of the electrolytic manganese investigation. He was supervising engineer of the Reno station at the time the investigations were made there. Mr. Shelton, who did a consideration amount of work, worked for Dr. Koster in

the Reno station. Mr. Royer also worked for Dr. Koster in the Reno station.

Q. And, as I understand it, that work which was done in the Reno station is described in R. I. 3406? A. That is correct.

Q. Who was the chief engineer on this project at Boulder City? A. The chief engineer at Boulder City was Dr. Koster, the chief engineer over Dr. Koster was Dr. Dean, who was the chief engineer of the metallurgical division, the Western Metallurgical Division.

Q. To your knowledge, were those men all familiar with the work that was being carried on at Boulder City, and I refer to Dr. Dean and Dr. Koster and Mr. Royer. A. They were all very familiar with the work.

Q. While you were with the Bureau of Mines, did Dr. Koster make any suggestion to you or to anyone else that you are aware of, in regard to the use of a metallic
44 salt such as ferrous sulphate for purification of the leached solution subsequent to the treatment of it with a xanthates or a hydrogen sulphide? A. He did not.

Q. Did Dr. Dean ever make any such suggestion to you? A. He did not.

Q. Were there any other skilled technical men in this field associated with you in the work that you were doing there at Boulder City in 1940 and 1941? A. Yes, there were several men. A Mr. Crowell, a Mr. Parkman, a Mr. Hunter, a Mr. Jacobs, Mr. Royer, were all technical men.

Q. And they were familiar with the work as it progressed, were they? A. That is correct.

Q. Intimately associated with it? A. With the exception of one man, Mr. Royer, who had worked on electrolytic manganese before, the other men had a wide field of experience but had never been in contact with electrolytic manganese until they started to work for the Bureau.

Q. My question was whether or not these men, whose names you have given, were intimately connected with the work that was being carried on at Boulder City after you

went there? A. Yes, they were directly assigned to
45 the work, directly assigned to the work.

Q. Over how long a period of time was this work carried on in the Bureau of Mines at Boulder City after you went there and prior to the time that you and Mr. Royer made the invention of the application? A. Between four and five months.

Q. Now, after you made the invention covered by the application involved here, what did you do with regard to testing it and using it? A. We started investigating its possibilities in the research immediately, over many, many tests and we found that it gave us the purification and control we were looking for. Therefore, we incorporated the idea into the flow sheet for the pilot plant and in November, 1941, when the pilot plant was started, the solutions were purified using this procedure.

Q. Now, will you please compare the results obtained after you started using the Woodman and Royer invention with the results which you had obtained at the Bureau of Mines in this work prior to that time? A. The result that we had obtained prior to the time of the invention, as far as a commercial unit is concerned, was an absolute failure. Upon the advent of this invention, we found that we could
46 plate solutions satisfactorily and continuously, therefore, it meant the difference between failure and a good operating plant.

Q. In your last answer, you said, "As far as a commercial unit is concerned." What did you have in mind in that regard? A. A commercial unit is a unit of high tonnage. It is a big plant, it is a plant such that you cannot have failure in the purification because if you do, you will spoil all of the manganese that is plating in a large cell room and if that happens, then you must recover all the cathodes, clean them in acid, polish them, clean all the cells, and start again, and with a normal operating crew, your plant would probably be down maybe from two, four, five days, and in a commercial operation you just cannot stand that kind of operation.

Q. Is that the kind of operation which you had at the Bureau of Mines prior to the making of your invention? A. No. Before the invention, we could plate for a few hours at a time, but we never knew from one purification batch to another, whether the solution would plate.

The Court: Whether it would what?

The Witness: Whether it would plate and deposit.

By Mr. Webb:

Q. So that, prior to the making of your invention, you got these inconsistent uncertain results, I take it? A. 47 That is correct.

Q. And afterwards, what did you get? A. Afterwards, we could plate with certainty.

Q. And prior to the making of your invention and the use of it in the Bureau of Mines work, did you have a degree of certainty which would have been satisfactory for any commercial operation? A. Before?

Q. Yes. A. No, absolutely not.

Q. Well, now, while you were doing this work at the Bureau of Mines, did you at any time take a solution which had not been treated by your process, try to plate with it, and then subsequently treat it with your process to see whether it changed the character of the results? A. We did that many times. We would take the solution from the hydrogen sulphide precipitation and try to plate that solution and it would not plate. We would give it the iron treatment and from there on the solution would be amenable—

The Court: Would be what?

The Witness: You could plate and deposit your manganese from the solution very satisfactorily.

By Mr. Webb:

Q. You spoke about the difficulties which you would 48 encounter if you had a process on the commercial scale that would stop plating from time to time. Approximately how long a period of time would your plant

have to be down in order to enable you to rehabilitate it and get going again? A. Depending upon a commercial plant, let's say forty tons per day of electrolytic manganese, I would say that your plant probably would be down at least four days, maybe five days. But even at the end of that time, if you were not sure that your solution would plate, you would not be sure that you could start the plant up again.

Q. Now, what, if any, effect on current efficiencies did the use of your process have? A. We found that the adoption of this purification step gave us higher current efficiencies, however it must be borne in mind that the current efficiencies that we obtained were good; whereas, on the other hand, there were so many failures that it is hard to establish what a current efficiency, overall current efficiency would be without using the invention.

Q. Will you explain what is meant by current efficiency and the significance? A. Current efficiency, to apply the term current efficiency is meant the amount of manganese that is actually deposited as against the amount of manganese that would theoretically be deposited. It is a term denoting that factor.

49 Mr. Webb: Will the reporter please read back that answer?

(The answer was read.)

By Mr. Webb:

Q. That is for a given quantity of current, I take it? A. Yes, that is for a given amount of electrical current passed through a solution.

The Court: That means the proportion of efficiency?

The Witness: Yes, you pass so much current through a solution, theoretically you should get so much, practically you only get so much, so if you divided the theoretical into what you get, that gives you your percent of current efficiency.

By Mr. Webb:

Q. The current efficiency that you are speaking about is the current efficiency in regard to the plating out operation, is it not? A. That is correct.

Mr. Webb: I just want to point up, Your Honor, that this matter of current efficiency is of no consequence so far as the purification of the solution is concerned, but then you take that purified solution and use it in the electrolytic cell and the current efficiency is quite important, because if it is low, well, naturally it increases the cost. We
50 are not referring to the efficiency of the current in connection with any of these purification steps which comprise the invention, but I am pointing this matter of current efficiencies out because it is one of the advantages which flows from the invention in addition to this extremely important matter of ability to continuously plate over a period of time.

By Mr. Webb:

Q. Now, Mr. Woodman, I wish you would compare the current efficiencies that you obtained prior to the making of your invention in this work at Boulder City, with the current efficiencies that you got afterwards, that is, after you adopted your invention. A. The current efficiencies we obtained before adopting the invention were very low, for the reason that we could not continuously deposit manganese, probably only for a few hours at a time. They would be in the order of nil, sometimes up to 50 percent, you never knew what current efficiencies you were going to obtain. After we started using the invention, our current efficiencies would run from an average of 50 to up to as high as in the 60 percents.

Q. Over, say, a 24-hour period, approximately what current efficiencies did you get? A. Over a 24-hour period, I would say an average of 55, 56 percent.

52 Q. I call your attention to R. I. 3681, which I will ask to have marked for identification as Exhibit No.

5.

(Plaintiff's Exhibit No. 5, Bureau of Mines R. I. 3681, was marked for identification.)

By Mr. Webb:

Q. I notice on page 22 of this publication, R. I. 3681, a statement that:

"When plating under the optimum conditions, an average current efficiency of 65 percent will be obtained over a 24-hour period."

Did you get such current efficiencies in your work? A. Yes.

Q. And referring again to this R. I. 3681, what is that? A. This is a Bureau of Mines report of investigations that was written by a Mr. Jacobs and myself when I was employed with the Bureau.

Q. What, if any, relationship does this report have to the work that you did while you were there? A. This report is a report on the studies in the electrodeposition of manganese and outlines the work which, up to that time, had been accomplished in the Boulder City research department. And for the first time, on page 10, for the first time that I know, the disclosure of the iron purification following the sulphide purification was made.

52 Q. And this R. I. 3681 correctly reports the work which you did? A. Yes, that is true.

Mr. Webb: I offer that R. I. 3681 in evidence as Plaintiff's Exhibit No. 5.

Mr. Cochran: Your Honor, there is no objection. This material was not offered before the Patent Office in the prosecution of the application. We offer no objection now, with the understanding that our failure to object does not admit any of the statements in here to be true or that it is pertinent to the issue.

The Court: I will admit it.

Mr. Cochran: We make no objection to its admission, with that understanding.

The Court: Very well. It doesn't mean necessarily that it is admitted as true, but it is taken in connection with the witness' testimony.

Mr. Webb: Yes, that is correct and that particular publication, Your Honor, the witness has stated that is a correct report of the work that was done.

(Plaintiff's Exhibit No. 5 was received in evidence.)

By Mr. Webb:

Q. Now, is this matter of current efficiency an important one, Mr. Woodman, in so far as operations are concerned; in other words, is it a matter of consequence?
53

A. Yes, the current efficiency of deposition is a very important factor. Upon the current efficiency depends the number of pounds of electrolytic manganese that a plant will produce in a day, and certainly upon those pounds of manganese depends the cost of operation and maintaining a plant.

Q. Well, now, was your process adopted by the Bureau of Mines prior to the time you left there? A. The Bureau of Mines adopted this process in their pilot plant when it first started out in November of 1941. I was there at the Bureau of Mines when that pilot plant commenced operations.

Q. And, if you know, did the Bureau of Mines continue to utilize your process after you left there? A. Yes, I lived in Boulder City, Nevada, while I was working for Basic Magnesium and I made frequent trips over to the Boulder City station, and they always did use in their pilot plant this invention.

Q. Did the Bureau of Mines, after your invention was placed in operation in the plant at Boulder City, revert at any time, so far as you know, to the old processes which were extant when you first went there? A. No, at no time
do I know where they reverted to their old processes.

54 Mr. Webb: Will you mark these Plaintiff's Exhibits Nos. 6, 7, and 8?

(Plaintiff's Exhibit No. 6, First Two Years Operation of the Bureau of Mines Electrolytic Manganese Pilot Plant at Boulder City, Nevada, was marked for identification.)

(Plaintiff's Exhibit No. 7, The Effect of Certain Variables on the Electrodeposition of Manganese, was marked for identification.)

(Plaintiff's Exhibit No. 8, The Effect of Cell Variables on the Electrowinning of Manganese, was marked for identification.)

By Mr. Webb:

Q. I show you a document which has been marked Plaintiff's Exhibit No. 6 for Identification. Will you please tell us what that is, Mr. Woodman? A. This is an article written by Mr. Jacobs, Mr. Hunter, Mr. Yarroll, Mr. Churchward and Mr. Knickerbocker, all men who worked and were working at the Bureau of Mines in Boulder City. The title is "First Two Years Operation of the Bureau of Mines Electrolytic Manganese Pilot Plant at Boulder City, Nevada."

55 Q. I show you a document marked Plaintiff's Exhibit No. 7. Will you tell us what that is, please? A. This is an article written by Mr. Jacobs, Mr. Churchward, and Mr. Knickerbocker, again men who had and were working with the electrolytic manganese at the Boulder City station. The title of this is, "The Effect of Certain Variables on the Electro-deposition of Manganese."

Q. I show you a document marked Plaintiff's Exhibit No. 8. Tell us what that is, please. A. This is an article written by Mr. J. H. Jacobs, who worked for and still is working for the Bureau of Mines at Boulder City. The title is, "The Effect of Cell Variables on the Electrowinning of Manganese."

Q. Does Mr. J. H. Jacobs, whose name appears on all these publications, is that Mr. Jacobs that you referred to a while ago as working on this project when you were at Boulder City? A. That is correct.

Mr. Webb: Your Honor, we have a stipulation here in regard to the introduction of these documents in evidence, and the stipulation also covers R. I. 3681, which is already in evidence. I would like to offer that stipulation as Plain-

tiff's Exhibit 9, and as Plaintiff's Exhibit Nos. 6, 7 and 8, I offer the documents which have been so identified.

The Court: They will be received.

56 (Plaintiff's Exhibit No. 9, stipulation dated October 18, 1950; and Plaintiff's Exhibits Nos. 6, 7 and 8, were received in evidence.)

By Mr. Webb:

Q. Now, I wish, Mr. Woodman, you would refer to Plaintiff's Exhibit No. 6, which relates to the first two years of operation of the plant at Boulder City, and tell us what that shows in regard to the adoption and continued use of your process by the Bureau of Mines in that pilot plant operation at Boulder City. A. This entire article deals with the first two years of operation of this pilot plant, and on page 408, column 2, the first paragraph, it states that:

"Pilot-Plant operations were begun in November, 1941, and have been continuous except for brief shut-downs for installation of new equipment. More than one-half million pounds of manganese have been produced."

On page 409, this last paragraph shows the procedure for the leaching and the purification of the solutions.

On page 410, which is a continuation of the paragraph on page 409, it states:

"It was found that if 0.1 gram of iron per liter of solution was added as copperas"—which is ferrous sulphate—

57 "and the solution was oxidized with air and filtered, all of the aforementioned materials were removed.

This was an important improvement, because it always ensured a pure solution for electrolysis."

That statement right there deals with the invention.

Q. Referring back to R. I. 3681, which is your own publication which you mentioned earlier and which is Plaintiff's Exhibit No. 5, do you find a similar statement in there as regards the addition of iron? A. Yes, on page 10, in the third paragraph a statement is made there:

"It was found that solutions treated in this manner were usually satisfactory for plating. However, this purifica-

tion method did not provide the degree of certainty necessary for a commercial operation."

That is referring to the old Bureau of Mines procedure. The next paragraph says:

"After extensive experimentation it was found that if 0.1 gram per liter of iron was added to the sulphide filtrate and precipitated as the hydroxide, the solution was cleared of all residual sulphides . . ."

Later, it says in the same paragraph:

58 "it has been proved by several months of laboratory operation that this final purification step definitely improves the solution for electrolysis."

The Court: What page are you reading there?

The Witness: Ten, sir.

By Mr. Webb:

Q. Now, referring again to R. I. 3681, which is your own report on the Bureau of Mines' work at Boulder City, and referring to page 2 particularly, that states there, does it not, that the process was then being tested on the 1,000-pound pilot plant at Boulder City? A. That is correct.

Q. And that was the fact? A. That is right.

Q. Now, referring to Plaintiff's Exhibit No. 7, which is the article entitled, "The Effect of Certain Variables on the Electro-deposition of Manganese," will you please tell us what that shows in regard to the adoption of your process by the Bureau of Mines and its continued use in the plant at Boulder City? A. Yes. In the second paragraph on page 383, under the title, "Introduction," it shows that more than one million pounds of manganese metal has been produced. And on page 384, in paragraph 3, in the fourth line from the bottom in paragraph 3, it states there that they are still using the invention.

59 Q. The copperas that is referred to in that paragraph, is what? A. Copperas is a name given for ferrous sulphate.

Q. Now, what is the date on that publication, Mr. Woodman? A. This was October 14, 1944.

Q. Now, will you please refer to Plaintiff's Exhibit No. 8, which was entitled, "The Effect of Cell Variables on the Electrowinning of Manganese," and tell us what that shows in regard to the adoption and continued use of your process by the Bureau of Mines? A. On page 440, the second paragraph, it shows now that 1,500,000 pounds of manganese metal had been produced, and in paragraph three, it shows that they are still using the invention in their pilot plant operations.

Q. And the publication is dated what? A. October 16, 1946.

Q. And how long had the work been carried on by that time, up to that time, including the research? A. How long had the work—

Q. Yes, by that I mean including the research preceding your invention. A. Well, the work had been carried on for approximately ten years total at that time by the Bureau of Mines.

60 Q. Are you familiar with the recommendations which are being made to industry by the Bureau of Mines as to the installation of electrolytic manganese plants based upon the work that had been done at Boulder City? A. I am.

Q. Will you please state what those recommendations are. A. The recommendations that the Bureau of Mines had made regarding a large-scale electrolytic manganese plant, capable of producing upwards of 40 tons a day of electrolytic manganese, were published in their Report of Investigations 3815. This report is quite complete, it gives the process, they have figured out the cost for the plant, they have also figured out the operating maintenance and other costs necessary for the production of 40 tons per day of electrolytic manganese. On page 17 of this report, it shows in paragraph three that they are still using the invention and have recommended its use in a large commercial operation.

Q. What is the statement there that leads you to that statement, Mr. Woodman? A. "The solution, after purifi-

cation with hydrogen sulphide, is essentially free of metallic impurities, but contains colloidal sulphur and colloidal metallic sulphides, which are removed by the addition of 0.152 grams of iron per liter of solution as ferrous sulphate, followed by oxidation and precipitation as ferric hydroxide."

61 Q. In other words, their recommendation is that the process to be used in this 40-ton-a-day plant, would involve the further purification of the solution by means of ferrous sulphate after the sulphide treatment?
A. That is correct.

Mr. Webb: Will you mark this Plaintiff's Exhibit No. 10?

(Plaintiff's Exhibit No. 10, the Hannay Patent, was marked for identification.)

By Mr. Webb:

Q. I show you the Hannay Patent, No. 2,259,418, which has been marked as Plaintiff's Exhibit No. 10. Have you read and are you familiar with that patent? A. I am.

Mr. Webb: I offer the patent, itself, in evidence, as Plaintiff's Exhibit No. 10, Your Honor.

The Court: I have a copy of it here. It will be received.
(Plaintiff's Exhibit No. 10 was received in evidence.)

Mr. Webb: That is the other principal reference relied on by the Patent Office. There is that Hannay Patent and that R. I. 3406 which describes the early Bureau of Mines work. Those are the two principal things.

Will you mark this, please?

(Plaintiff's Exhibit No. 11, flow diagram, Hannay Patent, was marked for identification.)

62 By Mr. Webb:

Q. Now, I show you Plaintiff's Exhibit No. 11, will you tell us what that is? A. This is a flow sheet that I prepared to show the steps followed in the Hannay Patent.

Mr. Webb: I offer the flow sheet in evidence as Plaintiff's Exhibit No. 11, and I also offer as Plaintiff's Exhibit No. 12,

an enlargement of that flow sheet. It is a little easier to read and possibly both the Court and the witness will prefer to look at it rather than the smaller sheet.

The Court: They will be received.

(Plaintiff's Exhibit No. 11, and Plaintiff's Exhibit No. 12, an enlargement of Exhibit No. 11, were received in evidence.)

By Mr. Webb:

Q. Now, Mr. Woodman, will you please describe for the Court the disclosure of the Hannay Patent? A. Starting with the leaching step, No. 3, sulphuric acid from the electrolytic cell immediately above it is mixed with ore in the leaching step No. 3. Here, the sulphuric acid leaches out the manganese and other impurities such as cobalt, nickel, arsenic, and iron.

After the leaching step, Hannay proposes to filter or remove the solution from the residue and he says remove
63 move the iron by standard methods, which is either by oxidation with air or with manganese dioxide. In removing the iron, he also removes the arsenic.

The Court: The what?

The Witness: He also removes the arsenic, because when you remove the iron and you oxidize it in a manganese sulphate solution, you will also remove the arsenic. The solution from Step 4 is passed to Step 5, where it is treated with hydrogen sulphide for the precipitation of metallic impurities. He proposes to separate the solution and the sulphide precipitate by some method of filtering.

He next takes the solution to Step 6 which is a crystallization step. Here, he proposes to crystallize out by heating the solution to from 80 to 102 degrees centigrade, he proposes to crystallize out manganese sulphate crystals. These crystals then are to be separated from the mother liquor and are to be mixed with solution from the cathode compartment of these electrolytic manganese cells. After the mixing and solution of the crystals, the solution is sup-

posed to be fed back to the cathode compartment of the cell. He shows at Step 6 where he takes the mother liquor from the crystallization step and he states that impurities, if you want to get rid of impurities, you may have to pass all of that solution back again through Step 5 in order to hold down the amount of impurities going to the electrolytic cell.

64 The crystallization Step 6, according to Hannay, is a further purification of solution. It is interesting to note that Hannay recognized a further purification after the sulphide treatment, Step 5, was necessary before the solution was passed to an electrolytic cell. However, the amount of equipment, the hundreds of tons of solution necessary, the amount of heat that would be necessary to heat the solution, it would be necessary to cool it back again, appears to make this process an uneconomical process to use in a commercial operation, and it has not been adopted in a commercial operation.

Q. In other words, the Hannay process has not gone into commercial use? A. It has not.

Q. You spoke about the fact that you would have to heat up large quantities of the solution if you were going to attempt to utilize a crystallization step such as that used by Hannay for further purification. Approximately how much liquid would you have to heat up and cool down per day in a plant, say the size of this 40-ton plant that you spoke of earlier, which was recommended by the Bureau of Mines? A. It would be necessary to heat in the neighborhood of several hundreds of tons of solution a day from his figure of 27 degrees centigrade up to 102 degrees centigrade.

Now, according to his procedure, it would be necessary to pass that solution back to the purification
65 step, therefore, he would have to cool that solution down because he states his purification must be made cold. And what he would be doing would be recycling a tremendous amount of solution, so he probably would be heating

and cooling up to perhaps a thousand tons of solution a day for the production of, say, 40 tons of electrolytic manganese.

Q. Would you consider those things as rendering the Hannay process commercially impracticable? A. I would say it would add tremendously to the cost of operating a plant.

Q. Now, will you please tell us the essential differences between your process and the Hannay process? A. The essential difference between Hannay's process and my process is in Step 6. Here, Hannay uses the crystallization step following the sulphide purification. We use the addition of copper sulphate at this point.

Q. Does Hannay disclose the step of treating the solution with a metallic salt, such as ferrous sulphate, after treatment of the solution with hydrogen sulphide, as in the fifth item on the chart? A. He does not.

Q. Now, will you contrast this crystallization step of Hannay's with the type of purifying treatment which you utilized following the hydrogen sulphide treatment
65 in your process? A. You want a comparison, is that right?

Q. Yes.

The Court: I think that would probably take some little time. I think we had better take it up tomorrow morning.

How much longer do you think it will take to dispose of this case?

Mr. Webb: I think, Your Honor, that we can finish in the morning.

The Court: Very well. Then I will take it up tomorrow morning again at 10:15. I have a little matter to dispose of first, I don't think it will take that long.

Mr. Webb: Thank you, Your Honor. Before we adjourn, may I just ask Mr. Woodman a point in order to correct what I believe was a slip? He used the term "copper sulphate" in one of his previous answers when he referred to the treatment following the sulphide treatment.

Did you mean by that "copperas"?

The Witness: Copperas ferrous sulphate.

Mr. Webb: Thank you, I thought that was what was meant.

(Thereupon, at 4:00 o'clock p.m., the trial was adjourned, to reconvene at 10:15 o'clock a.m., Friday, October 20, 1950.)

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IN THE UNITED STATES DISTRICT COURT
FOR THE DISTRICT OF COLUMBIA

Civil Action No. 3977-48.

VANADIUM CORPORATION OF AMERICA, *Plaintiff*,

v.

JOHN A. MARZALL, Commissioner of Patents, *Defendant*.

Washington, D. C.

October 20, 1950.

The above-entitled action came on for further trial on the merits before the Hon. Jennings Bailey, United States District Court Judge, at 10:15 o'clock a.m.

Appearances:

On behalf of the Plaintiff:

WILLIAM H. WEBB, *Esq.*,

BRUCE G. MACKEY, *Esq.*, and

DONALD A. GARDINER, *Esq.*

On behalf of the Defendant:

S. WILLIAM COCHRAN, *Esq.*

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PROCEEDINGS

Deputy Court Clerk: Vanadium Corporation of America v. Marzall.

Mr. Webb: Mr. Woodman, will you resume the stand?

Thereupon—**Frank W. Woodman**, the plaintiff, called as a witness in his own behalf, having been previously duly sworn, was examined and testified further as follows:

Direct Examination (Resumed)

By Mr. Webb:

Q. At the conclusion of yesterday's session, we were talking about the Hannay patent, and I believe, Mr. Woodman, you stated that Hannay does not disclose the step of treating the solution with a metallic salt after treatment of the solution with hydrogen sulphide, is that correct? A. That is correct, he does not.

Q. You mentioned this Hannay crystallization step, and I would like now for you to very briefly contrast that Hannay crystallization step with the ferrous sulphate purification step of your process. A. Hannay, in his crystallization step, proposes to purify his solutions by crystallization.

The Court: What is the number of that, No. 3?

The Witness: Step 3 in the Column 1 of Exhibit 17.

69 The Court: Very well.

The Witness: As I explained yesterday, this step would be a very expensive step in any commercial operation. As contrasted to Step 3 of Exhibit 17 in our invention, we add iron after the sulphide purification. This is a very effective and a very economical operation, and it has been put to use in a large-scale operation.

Mr. Webb: Will you mark this, please?

(Plaintiff's Exhibit No. 13, Flow Diagram, R. I. 3406; and Plaintiff's Exhibit No. 14, an enlargement of No. 13, were marked for identification.)

By Mr. Webb:

Q. I show you a chart which has been marked Plaintiff's Exhibit No. 13. Will you tell us what that is? A. That chart is one that I prepared showing the flow and the procedure used by the Bureau of Mines in their Report of Investigations 3406.

Mr. Webb: I offer in evidence as Plaintiff's Exhibit No. 13, the flow sheet just identified by the witness, and as Plaintiff's Exhibit No. 14, the enlargement of that. I

might say, Your Honor, that in the center column on the comparative chart Exhibit 17, you find similar steps to those which are shown on this chart which relate solely to 3406.

The Court: They will be received.

(Plaintiff's Exhibits Nos. 13 and 14 were received in evidence.)

70 By Mr. Webb:

Q. Now, referring to the chart, will you please state what the steps are which are disclosed in the R. I. 3406 publication?

The Court: Didn't we go over this yesterday?

Mr. Webb: No, Your Honor. We didn't go over R. I. 3406, which is one of the principal references relied upon by the Examiner. I went over it in my opening statement.

The Court: Well, maybe that is where I recall it.

Mr. Webb: That may be it.

The Court: Very well.

The Witness: No. 1 is shown as a Calcine Storage. That is the ore which has been reduced and has now been prepared for the leaching step, No. 2. Sulphuric acid is added to the ore in Step No. 2 in order to leach out the manganese from the ore. In so doing, other impurities such as the sulphates of iron, arsenic, copper, nickel, and so forth, are leached along with the manganese. This solution is filtered from the ore residue in Step 3. The ore residue in Step 4 is discarded as worthless.

In Step 5, iron is added to the solution. In the Bureau of Mines flow sheet, they added a small amount of iron when the iron in the solution was not sufficient to carry down the arsenic leached from the ore. The iron, arsenic, copper, nickel, are all present in the solution as sulphates. When the iron is precipitated, it carries down with it the arsenic. This step, however, does not precipitate the copper or nickel, because they are present in the solution as sulphates and as such the iron will have no effect on them.

71

The iron and arsenic are filtered from the solution in Step 6 and they are discarded in Step 7 because the precipitate is worthless.

The solution in Step 8 is treated with xanthate, xanthate is a soluble sulphide. The filtrate is treated with xanthate in order to convert the sulphates of nickel, copper, and so forth, into the sulphide form. In this form, they precipitate and are removed from solution in filter No. 9. However, some of those sulphides still remain in solution and are carried through the filter No. 9.

The solution from the filter No. 9 goes to the purified storage, No. 11, where sulphur dioxide is added to the solution.

The solution then is fed to the manganese electrolytic cell, No. 12, and here current again is passed through the solution contained between two electrodes and manganese metal being deposited on the cathode.

By Mr. Webb:

Q. Now, there has been some suggestion in the
72 Patent Office answer, that if you were to further treat, after Step 5 of this chart, with ferrous sulphate and further filter the solution in the condition that it is in in that Step 5 there and before the sulphide treatment, that you would accomplish the purpose of your invention. If you were to repeat that ferrous sulphate treatment, would you please tell us whether you would or would not accomplish the thing which you stated yesterday that you accomplished, namely, the removal of this copper, nickel, cobalt impurities? A. More iron could be added to Step 5, in fact, you could add as much iron as you wanted to at that step and it would, in no way, remove the copper or the nickel or any of the sulphides. You are adding iron at that step to a solution which is composed of the sulphates, and iron added to a solution containing nickel and cobalt sulphates will have no effect whatsoever upon those sulphates.

Q. Now, will you please state the essential difference between the process of R. I. 3406 and your own process? A. In R. I. 3406, the essential difference is that we add iron after the sulphide treatment. The Bureau of Mines does not add iron after the sulphide treatment and that is the essential point in the whole invention.

Q. Well, now, referring first to the Hannay patent which you have discussed and the Bureau of Mines R. I. 3406, do you find in either one of those any suggestion which
73 would lead you, as one skilled in this art, to add on to the processes disclosed there a ferrous sulphate or other salt purification treatment after the filtrate has been treated with hydrogen sulphide or xanthate or some other soluble sulphide? A. Absolutely not. They do not show that step.

Q. Referring again to Hannay and the Bureau of Mines publication R. I. 3406, do you find any suggestion in either of those that would lead you, as one skilled in the art, to add on that ferrous sulphate treatment to Hannay's process, either before or after the re-crystallization step? A. No, there is nothing in either the patent or the Report of Investigations that would indicate that you could use iron after the sulphide treatment.

Mr. Webb: Will you mark this, please?

(Plaintiff's Exhibit No. 15, the Jacobson Patent, was marked for identification.)

The Court: Xanthate is a sulphide?

The Witness: Yes, it is, it is a soluble sulphide. It is used a great deal in flotation work of ores. But it is a soluble sulphide and if you put it in a solution, it will go in a solution and will precipitate as sulphides any of the metals there which will form sulphides.

By Mr. Webb:

Q. I show you the Jacobson Patent, No. 1,137,005,
74 which has been marked Plaintiff's Exhibit No. 15.

Have you read and are you familiar with that patent?
A. Yes, I am familiar with that patent.

Mr. Webb: I offer it in evidence as Plaintiff's Exhibit No. 15.

The Court: It will be received.

(Plaintiff's Exhibit No. 15 was received in evidence.)

By Mr. Webb:

Q. Will you please tell us briefly what that patent relates to? A. This is a patent for a coagulant for water purification and the process for making same. It concerns a reagent form of aluminum sulphate and iron sulphate. Its sole purpose is to remove suspended matter from water, particles which are not in solution but are actually suspended in the water.

Q. Does that patent relate to or in any way describe any process for purifying manganese solutions? A. It does not.

Mr. Webb: That patent, Your Honor, was used by the Examiner in combination with one of the others and the Board of Appeals' decision said, "We don't think that is a proper combination at all."

The Court: I understood the Board of Appeals
75 disregarded this entirely.

Mr. Webb: That is correct, Your Honor. I think we don't need to dwell on it.

The Examiner also referred to a Prescott and Johnson article, which I would like to offer in evidence as Plaintiff's Exhibit No. 16.

(Plaintiff's Exhibit No. 16, an article by Prescott and Johnson, was marked for identification.)

By Mr. Webb:

Q. Do you have a copy of the article, Mr. Woodman? A. Yes, I have one here.

Q. You have read and are familiar with that article? A. Yes.

Mr. Webb: I offer it as Plaintiff's Exhibit No. 16.

The Court: It will be received.

(Plaintiff's Exhibit No. 16 was received in evidence.)

By Mr. Webb:

Q. What does that article relate to? A. This article relates to the precipitation or formation of arsenic sulphide when solutions containing arsenic are treated with hydrogen sulphide.

Q. Do you find anything in the article in regard to the purification of manganese solutions? A. I do not.

76 Q. Do you find in the article anything that would lead you, as one skilled in the art, to the use of the steps which you have described as being typical in your process? A. I do not.

Q. Now, the Examiner in his statement filed with the Board, and the Board of Appeals in its decision, held that if a manganese solution to be purified initially contained insufficient iron to effect proper precipitation of impurities, more iron could be added without invention. As a matter of fact, what would happen if more iron were added initially as suggested? A. That is in the first step?

Q. Yes. A. If more iron were to be added in the first step, it would not help to purify the solutions from nickel, cobalt, and such metals. It would merely be an additional agent, and would have no effect whatsoever upon those metals that we are trying to eliminate.

Q. Why? A. Because you are adding iron to a sulphate solution where all of the metals are present as sulphates, and as such, iron will have no effect upon the cobalt and nickel; whereas, if the iron is added to a solution which has been sulphided, then the iron will react and will remove those sulphides from the solution.

77 Q. In other words, you have to, as I understand it, you have to effect this conversion from the sulphate form to the sulphide form before the ferrous sulphate treatment will be effective to remove the impurities

that you have described? A. That is correct, that is the critical part in the entire invention.

Q. Now, the Patent Office Board of Appeals in its decision dated September 28, 1948, page 2, held that the current efficiencies obtained according to your method as given in Table 3 on page 8 of the specification are generally on the order of those obtained by Hannay. Will you please comment on that from the standpoint of its accuracy and correctness? A. No, they are wrong in that statement, for this reason: that the efficiencies as given in our invention are efficiencies over a period of hours of plating, 48 hours of plating; whereas, in Hannay, he merely states that he gets about 50 per cent efficiency but does not state any time of deposition whatsoever; whereas, in our invention, we claim we have efficiencies far greater than that.

Q. Referring to Table 3 more specifically, which appears on page 8 of your specifications, what are the current efficiencies that are set forth there? A. The current
78 efficiencies as set forth in this table for four individual tests are as follows: 54.2%, 51.95%, 55.51%, and 63.06%.

Q. And those were obtained over how long a deposition period? A. Over a period of 48 hours of deposition.

Q. And I believe you said yesterday that you got current efficiencies over like periods and longer periods, even up to 65%, possibly higher than that. A. That is correct.

Q. That is shown in your report that was prepared back in 1943 on this work? A. That is right.

Q. Now, on page 2 of the Board of Appeals' decision, the Board held also that the higher current efficiencies of 63.06, which is given in Table 3 for Test 4 in your application, was due to an increase in voltage and current densities and not to the method of purifying the solutions, and in that connection the Board also held that solutions 3 and 4 set forth there were identical. Will you please comment on those holdings from the standpoint of their factual accuracy or inaccuracy? A. The Board was in error in

that statement. The current densities as listed in Table 3 on page 8 are essentially the same for all practical purposes. The voltage as shown is approximately the same and

has no effect whatsoever upon the current efficiencies.

79 The thing that the Board overlooked, apparently, in making that statement was the fact that in Test No. 4 the ammonium sulphate concentration was 125 grams per liter. In Test No. 3, the ammonium sulphate was 149 grams per liter, and in Test No. 1 it was 174 grams per liter and in Test No. 2 it was 196 grams per liter.

At the time these tests were being made, we were also conducting tests to determine the efficiency of operation with varying ammonium sulphate concentrations, and the Board overlooked the fact that the ammonium sulphate concentrations in these tests were the ones that were varied and not the current density or the voltage. The ammonium sulphate concentration is of absolutely no effect whatsoever upon our invention, it works as well with a lower ammonium sulphate as with a high ammonium sulphate.

Q. Then, I understand your statement that the Board in that conclusion was wrong in two respects: First, in holding that solutions 3 and 4 were identical, is that right? A. They are not identical.

Q. And the Board was also wrong, I gather from your testimony, in holding that the difference was due to the differences in voltage and current density. A. The differences are not due to voltage and current density.

Q. There is one thing I probably should have asked you yesterday in regard to the importance of this metal, 80 manganese, that we are talking about. We have discussed it without saying anything regarding its importance or lack of importance in the nation's economy, and I would like to ask you whether or not it is a material which is of some consequence. A. Manganese is one of the most important metals that we have in the country, or actually what we need in the country. There is not a pound of steel made that does not contain some manganese. It is essen-

tial for the manufacture of steel; also, other high-grade alloys.

Q. Approximately how much is there in steel? A. That will vary, it will vary from .01 per cent, .05 per cent, maybe up to .2 per cent or .3 per cent, it depends upon the type of steel that you are making.

The Court: Any more used in steel used for armor, that is, tanks or ships?

The Witness: Manganese steel, yes. Manganese steel is used a great deal also where you have to have hard work surfaces like maybe the jaws of a crusher that is crushing ore, it seems to impart a property to steel that makes it tough and will resist abrasion.

By Mr. Webb:

Q. And in some of these higher alloy steels, how much manganese, approximately, do you have; in other words, what is approximately the top number that you run
81 into in regular practice? A. In various steels, it will amount to several per cent.

Q. Run up to 10 per cent, 12 per cent, is that what you mean, 15 per cent? A. That is right, it will vary 15 per cent to 12 per cent, depending upon the type of steel that you want.

Mr. Webb: Now, I mentioned, Your Honor, yesterday that the pleadings showed that a right had been granted to the Government under the invention. I just want to ask Mr. Woodman a question or two about that.

By Mr. Webb:

Q. Did you, yourself, and Mr. Royer grant to the United States Government a license under your invention? A. Yes, we granted to the United States Government a royalty-free license at the time.

Q. And under that license, I take it the Government is protected in regard to its requirement of manganese made under your process and irrespective of by whom made? A. That is correct.

Mr. Webb: Will you mark this, please?

(Plaintiff's Exhibit No. 17, comparison chart, was marked for identification.)

By Mr. Webb:

Q. I show you Plaintiff's Exhibit No. 17. Will you
82 tell us what that is? A. That is a chart that I prepared in order to show the steps involved in the Han-nay process, the Bureau of Mines' process as in R. I. 3406, and those involved in our invention.

Mr. Webb: I offer this chart in evidence as Plaintiff's Exhibit No. 17.

The Court: It will be received.

(Plaintiff's Exhibit No. 17 was received in evidence.)

Mr. Webb: I also offer as Plaintiff's Exhibit No. 18 the enlarged chart which I believe Your Honor has.

The Court: It will be received.

(Plaintiff's Exhibit No. 18, an enlargement of Exhibit No. 17, was received in evidence.)

By Mr. Webb:

Q. Now, referring to that chart, Mr. Woodman, as I understand, it shows the principal steps which are involved in those three processes, is that correct? A. That is correct.

Q. Now, referring to the first two steps in each of those processes, are they substantially the same? A. The first two steps in all three of the processes are essentially the same.

Q. Well, now, referring to Step 3, as shown in that chart,
is that step as shown for the Woodman, et al., inven-
82 tion as shown there, the step which you have referred to as the ferrous sulphate or iron treatment which follows the hydrogen sulphide treatment? A. I am sorry, I didn't get the question.

Q. My question is merely this: Is Step 3 as illustrated here in the right-hand column, the step which you have referred to heretofore as being the ferrous sulphate treat-

ment step which comes after the hydrogen sulphide treatment step? A. That is correct.

Q. In other words, just to point up the matter, it is the second and third steps in the sequence which is set forth in the chart which are, I believe, as you put it earlier, critical in your process? A. The sequence of those steps is the critical part of the invention.

Q. Is there any step even comparable to Step 3 of your process in the Bureau of Mines' R. I. 3406 process? A. No.

Q. Is this third step of your process, as shown on the chart here, disclosed in or suggested by Hannay? A. It is not.

Q. Now, in your testimony, you have emphasized the fact that your ferrous sulphate treatment follows after a hydrogen sulphide treatment of the solution. Is that a matter of importance that that step follow after the hydrogen sulphide treatment? A. Yes, that is the important step, it is the critical step in the process.

Q. Yesterday, the Solicitor for the Patent Office stated that in such processes as we are talking about here, the sequence of steps may or may not be important. What are the facts in regard to the importance of the proper sequence of steps in your process? A. The sequence of these steps is very important. They are the critical part of the entire purification program.

Q. Now, the suggestion has been made by the Patent Office that if you do not get all of the arsenic out in the first step of these processes, it would not constitute an invention to treat the solution again to take it out. If you were to treat the solution again with ferrous sulphate as suggested prior to Step 2, as shown on the chart, would you accomplish the removal of the impurities removed by your process? A. No, you would not remove the impurities that we remove by following the sulphide purification.

Q. Now, yesterday the Solicitor for the Patent Office also stated that R. I. 3406 is not limited to any particular sequence of steps. I wish you would refer to that article which is in evidence here as Plaintiff's Exhibit No. 4, and

85 particularly to the flow chart opposite page 6 and tell us what it shows in regard to the sequential steps. A. The Bureau of Mines in their Report of Investigations 3406, very definitely sets out their procedure for the purification of the solutions.

Q. And the sequence is iron and oxygen treatment to remove arsenic before the hydrogen sulphide treatment?

A. That is correct.

Q. I want you to refer also to page 8 of R. I. 3406, which describes the purification procedure, and more particularly, the part down near the bottom of the page which says:

"The solution from the filter flowed into a second lead-lined tank and was treated with a mixture of 0.3 gram per liter of sodium ethyl xanthate and 0.2 gram per liter of potassium pentasol xanthate. The solution was stirred by hand to obtain complete dissolution of the reagents, and six hours was allowed for complete reaction of the xanthate to precipitate cobalt and nickel."

In addition, I think you might refer to the immediately preceding sentence or so, that is, the sentence or so preceding what I just read, and tell us what that says specifically in regard to the sequence of steps. A. The sequence as outlined by the Bureau of Mines says, first, treat the solution obtained from the ore with iron in order to remove the arsenic, and if not enough iron is leached
86 from the ore, add enough iron to be sure that the arsenic is removed.

The second step in their flow sheet says that they add Xanthates to precipitate the copper and the cobalt as the sulphides.

Q. Is there any suggestion there that you can alter that sequence of steps? A. They make no suggestion about altering that sequence of operation.

Q. Is there any suggestion there of a ferrous sulphate purification treatment after a soluble sulphide treatment?

A. There is no suggestion made to that effect.

Q. In any of this work of the Bureau of Mines as reported in R. I. 3406, or in the work done by you with the Anaconda

Company which I believe you stated was based upon R. I. 3406, or in any of the work done or the literature published prior to your invention, was there any suggestion at all of using a ferrous sulphate treatment after a hydrogen sulphide or xanthate or other soluble sulphide treatment? A. To my knowledge there has never been any suggestion by the Bureau of Mines, or men in the Anaconda organization, or to my knowledge anything published in the literature which would indicate that ferrous sulphate should be used after a sulphide treatment.

Mr. Webb: You may cross-examine.

87 Cross-Examination

By Mr. Cochran:

Q. Mr. Woodman, referring now to the Hannay patent, Hannay et al. patent, that shows all the steps in your process claims except the final step of adding metallic sulphate, the Hannay patent shows all the steps leading up to this final step of adding the metallic sulphate? A. Leading up to the final step, that is right.

Q. And the Bureau of Mines publication No. 3406 does show the addition of ferrous sulphate to a manganese sulphate solution in order to remove an impurity? A. In order to remove arsenic.

The Court: To remove what?

The Witness: Arsenic.

By Mr. Cochran:

Q. Then, considered individually and in no particular sequence, we can then say that all of the steps of your process are old in the prior art? A. Absolutely not.

Q. The steps now considered not in any particular sequence and not in any particular combination, but considered individually, are old? A. No, absolutely not.

Q. Well, we have established that the Hannay patent shows the preliminary purification up to this final
88 ferrous sulphate addition? A. Yes, it shows ferrous sulphate addition at the start.

Q. And, we have established that the Bureau of Mines publication 3406 shows ferrous sulphate addition to manganese sulphate solution? A. At the start, the same as we do. All three are identical at that stage.

Q. Then, we can say that, not considering the sequence of the operation, the steps individually are old in the art?

A. I might explain that. The step that you are talking about which is the addition of iron to a manganous sulphate solution, or the addition of iron to a zinc sulphate solution in the electrolytic industry for the sole purpose of taking out arsenic, is old. Hannay used an old process there, the Bureau of Mines used an old process, we used an old process as the first step, and it is for the purpose of the removal of arsenic, that has been known to the industry, oh, since maybe 1916 or 1918. But that step is made to a solution which contains sulphates and its sole purpose is the removal of arsenic, it is not capable of removing anything else at that stage. But it is an old process for the removal of arsenic, but in our process where we add iron again we are not concerned with the removal of arsenic. We have accomplished that in the first step, therefore, arsenic is of no concern to us in our Step No. 3.

89 Q. That is the point that I wanted you to make, the fact that it is for a different purpose. It is the same step but for a different purpose and in a different sequence of operations. A. We are using iron in the third step for a totally different purpose, a completely and totally different purpose, a reagent which is supposed to and will perform a different chemical function entirely than Hannay or anyone else does in the first step.

Q. Now, I would like to take you back, if I can, to your state of mind at the time that you conceived your process just prior to that. You then were faced with this solution which had been subjected to a number of purifying operations, but still it didn't plate. Your problem was to treat it so that it would plate. That is correct, isn't it? A. That is correct. We were faced with a pilot plant, a large-scale

operation which was going to start in a very few weeks. We had used the Bureau of Mines' process, and had abandoned the xanthrate treatment as being unsatisfactory. The Bureau of Mines had converted at that time to the use of hydrogen sulphide instead of xanthrate and the process still would not work on a commercial basis. Therefore, we were faced with trying in a few weeks to start a plant with a process that would not work commercially.

Q. Did you know what the impurities were in this
90 material which were inhibiting the plating? A. No, we did not know that. It must be realized that a laboratory, in order to detect impurities, very minute impurities, it is nearly impossible sometimes for a laboratory to find out all of the elements that are in a solution. Yet, an electrolytic cell is so sensitive, so sensitive to impurities, even impurities that the laboratory themselves cannot detect, that it will ruin deposition, it will ruin deposition entirely. We did not know at that time everything that was causing our trouble.

Q. But you did suspicion that it was colloidal matter or traces of sulphides not removed by the preceding operations, you suspicioned that? A. We suspicioned that there was something, we knew, shall we say, not suspicioned, we knew something was coming through that was harmful, but we certainly had no idea what it was.

Q. You had some reason to believe that there might be arsenic in there, didn't you? A. I had no reason, in fact, the fact of the matter is all through the years of electrolytic zinc plant operations and all, the first step where we add ferrous sulphate to remove arsenic has always proven very successful. We had no reason to believe it was arsenic. In fact, arsenic was the farthest thing from our minds.

Q. You were familiar with the material stated in
91 the Prescott and Johnson book to the effect that hydrogen sulphide treatment would not necessarily remove all the arsenic? A. According to that article, on certain solutions performed in certain ways, not according to the way that we worked our sulphide purification, it may

be possible that arsenic might not be precipitated by the sulphide treatment. But here is the point, we removed arsenic thoroughly before the sulphide treatment, therefore, the article in Prescott and Johnson has no significance to our invention.

Q. As a matter of fact, the evidence presented here shows that the first iron treatment did not remove all the arsenic, doesn't it? A. I don't know of any such evidence.

Q. I would like to refer you to Plaintiff's Exhibit No. 6, "The First Two Years' Operation of the Bureau of Mines Electrolytic Manganese Pilot Plant," page 412, the second column, the second paragraph. I wonder if you would read the first three sentences. A. Let me see if I am correct.

Q. It starts, "Although the solution—" A. "Although the solution is now free of metallic impurities, it contains colloidal sulphur, colloidal metallic sulphides and organic matter that is introduced with the ammonium sulphate.

These materials are removed by adding copperas and oxidizing the iron with air. The iron precipitates as ferric hydroxide; this precipitate absorbs the sulphur and colloids and also removes any residual arsenic and molybdenum that were not precipitated by hydrogen sulphide."

Q. Does that step that is referred to of adding copperas, is that the step, the final step in your process? A. I believe it is, but I would have to go back and check for sure before I make that statement. But I believe that is correct, that that addition of iron at that step is the one where we have the invention.

Q. And it does state that it removes arsenic? A. It says it also removes any residual arsenic. You don't know whether there is arsenic there or not. It says any residual arsenic. It does not come out and say that it removes arsenic in that step.

Q. As a matter of fact, you know just as much about arsenic being in there, or you knew at the time you filed this application, as you knew of any of these other impurities, didn't you? A. No, because the iron purification as out-

lined in Step 1 of both or all three processes, removed the arsenic satisfactorily. And it had been proven through years of experience in other zinc work that it did. Now, may I refer you to one thing on what you are quoting
 93 here in this?

Q. Yes, go ahead. A. Could I show this to the Court?

The Court: Yes.

The Witness: And I will show you why they make that statement in this article. They take the leach solution from the calcine, since our invention the Bureau of Mines has done this, they have and recommend now that they eliminate Step 1 as shown on the Bureau of Mines report 3406. Now, then, they go directly to a hydrogen sulphide purification as noted right here (indicating). Here is where your solution comes off the leach tanks, it goes to a thickener and the overflow from the thickener goes directly to the hydrogen sulphide purification, so they eliminate entirely Step No. 1.

Now, after Step No. 1, the hydrogen sulphide purification, then they add our invention which is to add iron to the sulphide purification solution. Now, they have let your arsenic come on through and they have caught some of it in the sulphide purification, but they have found if they use our invention that they can eliminate this first step. That is why the statement is made and the one you had me read, right over here (indicating), that in the event a little arsenic comes through, don't worry, because the iron treatment after sulphide purification will take it.

In other words, what they have done is actually
 94 find that this invention of ours eliminates the necessity of their first step and where we add our iron, it not only accomplishes the purpose of removing the sulphides from the solution, but if they do let a little arsenic slip through, it doesn't hurt them. Therefore, our invention has actually improved the process.

Do you see what I am getting at?

Mr. Cochran: Yes, exactly.

The Witness: In other words, we are quoting from here now, understand, and your article that you read in here is totally different than what we are discussing with Hannay or 3406. But they are still using our process for the purpose it was invented for, but they now still rely on it to take out arsenic, where we did not. But it will still do it. But they are using our process for exactly the purpose we invented it for.

By Mr. Cochran:

Q. Then, you might say that they are using this final step, the addition of ferrous sulphate, for the same purpose it is disclosed in 3406, at least partly for that purpose?

A. No, definitely no. No, because in the first step now, understand, here is the critical part of this whole thing. In the first step, they add iron to a sulphate solution, everything is there as sulphates. Iron has the effect to bring down arsenic in the sulphate solution, but it has
 95 no effect to bring down copper or nickel or the rest of them in a sulphate solution. So, we sulphide that solution, we put the metals in a different chemical compound and in that state we add iron again, and now we can clear the solution of all of the sulphides.

So, your arsenic now—according to Prescott and Johnson, the article which you brought up a minute ago, shows that now we have already converted the arsenic over to the sulphide. Therefore, we will remove it with the cobalt and nickel in the same mechanism.

The Court: Is the process used in that way, the improvement in your process?

The Witness: It is our process, sir; it is our process.

The Court: By omitting the first step, is that an improvement?

The Witness: Absolute improvement, a definite improvement which will save hundreds of dollars in a year's period of operation.

The Court: Very well.

The Witness: Because they have taken our invention now which has proven to be a commercial step, one that ensures deposition, and they have found also, through a period of time, that by using that step after the sulphite treatment, they can eliminate a step up here now that formerly cost them a lot of money.

96 By Mr. Cochran:

Q. Now, referring to Plaintiff's Exhibit No. 7, page 384—"The Effect of Certain Variables on the Electro-deposition of Maganese"—the third full paragraph, the last sentence says, starting, "After the precipitated—". I will read it into the record to save time:

"After the precipitated sulphides are removed by filtration, 0.1 gram per liter of iron as copperas is added to the solution and oxidized and precipitated. The ferric hydroxide precipitate removes any residual arsenic, as well as colloid sulphur and sulphides."

* * * * *

97 By Mr. Cochran:

Q. I suppose your comments there would be the same as in connection with the article which we just referred to? A. That is correct, because they have now gone to using our invention in the step and eliminating the first; therefore, they may have arsenic or may not, coming through. But if there is some, we not only take out the cobalt and nickel but we will also take out anything that comes through like arsenic.

Q. Well, you have reason to believe that since these sulphides were insoluble, I know you spoke of them as being in solution, in the sulphate solution, but actually they are insoluble and are suspended as colloids? A. No, that is a statement that has been made constantly throughout this entire procedure. There is nothing insoluble. We don't know today, I don't believe, of any sulphide or any material which we can say is totally insoluble in any solution.

In fact, we know that sulphides of the various metals have definite solubilities in certain solutions and are present in solution and not present as suspended material or as colloids. We know there is definite solubility for that kind of compounds.

Q. However, in your specification, you do state that probably these impurities are present in the form of colloids, do you not? A. In our specifications, we state
98 that we do not know the exact mechanism of this purification, that there may be some colloids in that. We also state it is also of a chemical nature in our specification.

Q. You do state that there is certainly a possibility that they are in the form of colloids? A. There is a statement to that effect in the specification.

Q. And it was well known, wasn't it, at the time that you conceived this invention that the addition of iron salt to solution would tend to form iron hydroxide and carry down with it impurities of that type; that was a well-known possibility, wasn't it? A. Iron and alumina, according to your patent by Jacobson have been used for years and years in water treatment for the removal of suspended particles. However, our iron treatment that we gave this solution—we were not so concerned with the colloids, as you call them, as we were of the chemical reaction that was taking place, and I will tell you why. We would take the solutions, prior to putting them through an electrolytic cell, the solutions would not plate before the iron treatment. We would take those solutions and many times filter those solutions through paper pulp an inch thick, try to plate them, filter
99 them again through paper pulp an inch thick, which you know is one of the finest filtration aids that you can get, and still those solutions refused to plate, which was certainly indicative that it was not suspended matter or colloids like that that was doing it. It must have been some chemical compound in the solution that the filter could not touch.

Now, we could take those solutions, treat them with our iron, filter, and the solutions would plate beautifully.

Q. In other words, it definitely is a chemical action, you maintain? A. That is what we believe.

Q. Does your specification state that? A. Our specification states it may be of a chemical nature.

Q. As a matter of fact, it says the purification, however, may be in part chemical. A. That is right, may be in part chemical, that is what we believe.

Q. It also states, does it not, the tendency of metal sulphides to form colloids is well known and free sulphur may be postulated as present in the solutions? A. That is right.

Q. And that free sulphur would be in what state, a colloidal state? A. Oh, free sulphur, I believe, I don't know whether you would call it colloidal, I don't think you
100 would call it colloidal because if you get free sulphur in a solution, you can see it readily and lots of times it will come to the top as a sort of a scum. It is just your definition of a colloid and a suspended particle. Actually, for the purposes of what we are discussing, I don't think it makes any difference.

Q. In other words, your specification does state that at the time you conceived this invention, you thought that there might be free sulphur suspended in the solution? A. Yes, according to the specification, there were several things things that we put in there, colloidal sulphur, colloidal material, but we believe it was of a chemical nature, because as I just got through explaining, we had filtered it through the finest filtration equipment that we could filter, which should have caught suspended materials. We not only filtered once, we filtered it many times to try to get a solution to plate.

Q. But your specification states that the action might have been chemical, but the particles might have been cel-loids? A. We believe it to be of a chemical nature due to the experimental work that we had, we believe it to be of a chemical nature.

Q. But you did not state that to be a fact in your
101 specification? A. We, in our specification, stated that we believed it to be of a chemical nature.

Q. Well, it was well known, wasn't it, to an expert in the chemical art that the use of iron sulphate would precipitate colloidal matter? A. Oh, you can go back through the literature, in fact, you brought up one patent here that—

Q. Your specification even states that? A. For colloidal material, but as I say, I don't feel that we are dealing that way as much, and it is stated in the specification it is of a chemical nature and not of a colloidal and of suspended material, we believe it now to be of a chemical nature. At that time we did not have the laboratory equipment, the fine laboratory equipment which is necessary to analyze solutions as accurately as we have now. But in our specifications, we covered the possibility and we said we believe it to be of a chemical nature.

Q. I believe that is an important point and I would like to make it clear that your opinion as to the nature of these impurities has changed since this specification was written. Now, you believe that the material is an actual solution, whereas then you did not know. You said the action may be chemical in part, however, the tendency of sulphides to form colloids is well known and free sulphur might be in the solutions. That states your frame of mind at the
102 time you wrote the specification, isn't that correct, and your opinion now has changed as to that? A. I don't believe that my opinion has changed in this respect. I believe exactly what is written in the specification and I believed then and I believe now that the function of the iron in our invention is of a chemical nature.

Q. I would like to ask you if you feel your last statement is in accord with the passage from the specification which I have read. A. I believe my statement is in accord with the specifications because in the specifications we claimed there that we believed there could be import of a chemical nature, we also listed several other things. We believed at that time that this addition was of a chemical nature. I believe today that it is of a chemical nature.

Q. Well, that doesn't concern us. Now, I would like to go on to the disclosure in the Bureau of Mines report.

The Court: I will take a ten-minute recess.
(A short recess was taken.)

By Mr. Cochran:

Q. I would like to refer you now to the Bureau of Mines Report of Investigation No. 3406. In that report on page No. 7, there is a title, "Impurities in Manganese Electrolyte," and subtitles of Iron, Arsenic, Copper, Cobalt, and Nickel. Now, in connection with each of those, the article discusses methods of removing those impurities from the solution. Isn't that true? A. That is true.

Q. In connection with the one labeled arsenic, do you find any indication there, in that paragraph, that the removal of arsenic by ferrous sulphate must precede the other purification steps which are mentioned? A. This article merely states what is already well known to the art, that arsenic can be removed by iron. This merely states something that has been known in the zinc industry for many years.

104 Q. There is no indication there that it has to take place before any of these other purification treatments which are mentioned? A. He does not state that in this paragraph, but in the flow sheets in Article 3406, he definitely states where he is to make his purification for arsenic.

Q. To what portion of the article are you referring now? A. That is Figure 2, called "Flow sheet for leaching ore and purifying leach solutions at the experimental pilot plant," and he definitely says exactly where he adds his iron for the removal of the arsenic and that is in line with the teachings that have been known for years.

Q. Now, that flow sheet, does that correspond generally to the description which is given under the title, "A Purification Batch," on page 8? Just generally, I don't mean in any detail? A. In general, in general, yes; because his first step is iron is added. He filters, the next step he adds the xanthates.

Q. He refers to this purification batch as a typical purification batch, doesn't he? A. Yes, referring to a typical purification batch.

Q. So that he is not necessarily limiting his disclosure simply to that particular sequence of events? A.
105 Yes, I would say he is, because he stated directly in his flow sheet and in all his publications exactly step by step the way he did it and the way he recommended it being done.

Q. Is there any indication in this Bureau of Mines publication particularly in connection with the removal of arsenic, that the use of ferrous sulphate would not remove small amounts of arsenic, residual amounts? A. He states in here that the concentrations of arsenic—it was found that so much iron would reduce the arsenic content from so to so. He does not state that iron will completely eliminate arsenic from the solutions, because that is an impossibility, an absolute impossibility, to state that we completely eliminate something from solutions. Our analytical tests, as good as they are, could never prove that statement.

Q. So even your process won't completely eliminate the arsenic? A. Our process is not concerned with the removal of arsenic. Our process is concerned with the removal of metals after a sulphide purification. We have successfully removed arsenic in Step 1. We are not concerned with the removal of arsenic in our invention.

Q. This reference then, I take it, coming back to a prior question, does not teach that you could not remove
106 small amounts of arsenic as well as the larger amounts mentioned by the use of ferrous sulphate; in other words, the reference does not teach away from removing residual amounts of arsenic? A. It all depends on what a man wants to call residual. Now, as I say, Shelton or Hannay are merely adopting a procedure which had been known for years and which had worked very successfully, very successfully, in the removal of arsenic from solutions for the electrodeposition of zinc. So his procedure

here has been copied from an identical procedure that had been in use for years and years very successfully.

The Court: Do any of these processes leave manganese absolutely pure?

The Witness: The manganese solutions?

The Court: Yes, in other words, is the final result free from all of what you might call impurities?

The Witness: Oh, no, no. That would be an impossibility, I believe. I don't know of any procedure that you could say that if we add this, we will eliminate everything but the manganese. But we do try to add this to eliminate the bulk, shall we say, of the impurities which will interfere with the deposition of manganese, and the lower that we can reduce those impurities, the better the deposition, the greater the current efficiency. But I don't believe
107 there is a case in history where you can say, "I have eliminated everything but what I want," I don't believe so.

The Court: Very well.

Mr. Cochran: I think that is all.

Mr. Webb: That is all, Mr. Woodman.

(Witness excused.)

Mr. Webb: I have one more witness, Your Honor, Mr. Parkman.

Thereupon **Howard Calvin Parkman** was called as a witness by the plaintiff and, having been first duly sworn, was examined and testified as follows:

Direct examination

By Mr. Webb:

Q. Will you please state your name, age, and residence, Mr. Parkman? A. Howard Calvin Parkman, age 42 Niagara Falls, New York.

Q. And now, will you please state the advanced education that you have had? A. I obtained the Bachelor of Science Degree in Metallurgical Engineering in 1934, and the

Master of Science Degree in Metallurgical Engineering in 1935, both from the State College of Washington, Pullman, Washington.

Q. Now, after graduation in 1935, after getting
108 your Master's degree, what was it you did? A. I was employed by the Government in the State of Washington in development research directed toward the utilization of certain raw materials that had not been, at that time, exploited in the Pacific Northwest.

Q. And did that work you were doing for the State Government of Washington involve purification of different types of solutions and flotations, for example, of magnesite? A. Yes, we were working with the preliminary work directed toward the production of magnesium, there was a large amount of that ore in the Northwest, as well as certain refinements to copper metallurgy, production of alumina for the manufacture of aluminum from large deposits of then not commercial raw materials located in the Northwest.

Q. And you continued in that work until December, 1936, I believe? A. We continued that work until December, 1936, at which time the appropriations that had been granted by the Government of the State of Washington had been depleted.

Q. And after leaving that work, with what company did you go? A. I then took a position with Vanadium Corporation of America at Bridgeville, Pennsylvania, in their research and development division.

109 Q. And how long did you remain with the Vanadium Corporation? A. I remained at that position from January, 1937, until February, 1941.

Q. And where did you go when you left in February, 1941? A. In February, 1941, I accepted a position with the United States Bureau of Mines at Boulder City, Nevada.

Q. And what were your time and efforts devoted to in this work with the Bureau of Mines at Boulder City? A. I was assigned to the problem of purification and develop-

ment processes and their application to production of electrolytic manganese and the pilot plant which was then being designed and built.

Q. Now, when did you leave the Bureau of Mines? A. I left the Bureau of Mines in December, 1941.

Q. And where did you go after leaving? A. I returned to the Vanadium Corporation of America at Bridgeville, Pennsylvania.

Q. And what was the the nature of the work that you did at Bridgeville, Pennsylvania, for the Vanadium Corporation of America at that time and also on your previous occupation? A. Development processes and production of processes related to ferroalloys.

Q. And you stayed at Bridgeville until about 1943,
110 did you? A. I remained at Bridgeville until 1943, yes.

Q. And then I believe you went to the Niagara Falls plant of the Vanadium Corporation of America? A. I was transferred to the Niagara Falls plant in August, 1943, as reduction superintendent. That term is not commonly used, it is in most plants called production superintendent, but in our company that term was used.

Q. And you were reduction superintendent for how long a period of time? A. Until 1947.

Q. And what is your present position you hold? A. At present, I am general superintendent of the Niagara Division of Vanadium Corporation of America.

Q. And what are the principal products made at that division? A. The principal products we make are, of course, ferroalloys and metals, ferrochromium, all the grades of ferrosilicon, ferrotitanium, alloys of manganese, chromium, silicon, and various combinations, in fact all of the principal ferroalloys used subsequently in manufacture of alloy steels.

Q. Now, going back to your work at the Bureau of Mines in 1941, I believe you said that that was related to the purification of manganese salt solutions and the elec-

111 trodeposition of manganese. Is that right? A. That is right.

Q. To whom did you report at that time? A. Dr. Koster.

Q. Now, what process was in use at that plant when you went there? A. They were utilizing the process that had been originally prepared covering roasting, reducing roasting followed by leaching with one exception, that they had replaced the xanthates precipitation with hydrogen sulphide.

Q. And the process that you are referring to is that one that is described in R. I. 3406, modified in the manner in which you have just stated? A. Yes, sir.

Q. What process was used there when you left there in December of 1941? A. The process used at the time I left the Bureau of Mines was further modified by the addition of the process of purification after hydrogen sulphide treatment by the use of iron as developed by Mr. Woodman and Mr. Royer.

Q. So, when you left there in December, 1941, the Woodman and Royer process was in use? A. That had been in use, yes, sir.

Q. And they abandoned the previous process, the process of R. I. 3406 and the modified process of 3406 involving the substitution of hydrogen sulphide for the xanthates? A. Yes, sir.

112 Q. Now, will you please compare the results obtained at the Boulder City plant prior to the adoption and use of the Woodman and Royer invention, and those obtained after its adoption and use? A. The electrodeposition of manganese prior to the adoption of the Woodman and Royer process, was most discouraging. We obtained no consistent results. We had no assurance that any solution would work. We did for a short time, of course, obtain deposits, but with no consistency from one batch of solution to another. It was not until the adoption of the Woodman-Royer process that we obtained results that were consistent and satisfactory.

Q. Are you familiar with the Hannay, et al., patent, No. 2,259,418? A. Yes, sir.

Q. And you had read that, had you? A. Yes, I have read that.

Q. All right. Do you find in that patent any suggestion whatsoever of the use of a ferrous sulphate addition or purification step following a sulphide treatment in the purification of manganese, which solutions are used for electrolytic manganese depositions? A. There is no such reference.

113 The Court: Isn't this testimony a repetition of the preceding witness?

Mr. Webb: To that extent, yes, Your Honor, to a slight extent. The purpose of it is just this. Mr. Parkman is a highly skilled technical man and I want to show that to him as a skilled man, there is no suggestion in this prior art.

The Court: Very well. I am not trying to cut you off. I thought if it was simply a repetition of the preceding witness' testimony, it was not much needed.

Mr. Webb: Just two or three questions will be a repetition, Your Honor, but that is my purpose.

The Court: Very well, proceed.

By Mr. Webb:

Q. Is there any suggestion of that character in the Bureau of Mines R. I. 3406? A. There is none.

Q. Is there any suggestion in either of those two references or in any of the other references which have been discussed here in court the last two days, of the step of adding iron as a ferrous sulphate, or the like, to a sulphide solution? A. There is not.

Q. In the work that you were doing at the Bureau of Mines Boulder City plant, did it occur to you that the difficulties which you were encountering could be eliminated by the addition of ferrous sulphate to a sulphide solution? A. It did not occur to me, no, sir.

114 Q. Did it occur to you at any time during the work that you were doing for the Bureau of Mines at Boulder City on this specific problem, that your problems could be solved

by the use of a ferrous sulphate purification treatment following a hydrogen sulphide treatment of the solution? A. It did not occur to me, no, sir.

Mr. Webb: That is all. You may cross-examine.

Mr. Cochran: I don't think I have any questions.

The Court: Step down.

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Filed Nov 21 1950

UNITED STATES DISTRICT COURT
FOR THE DISTRICT OF COLUMBIA

Civil Action No. 3977-48

VANADIUM CORPORATION OF AMERICA, *Plaintiff*,

v.

JOHN A. MARZALL, Commissioner of Patents, *Defendant*

The Opinion of Judge Bailey.

This is an action under R. S. 4915 brought by the Vanadium Corporation of America, in which it asks the Court to authorize the Patent Office to issue a patent on Woodman and Royer Application, Serial No. 430,258, filed February 10, 1942.

The invention is now owned by the plaintiff but its ownership is subject to a royalty-free license which was granted by Woodman and Royer to the United States Government.

The invention relates generally to the manufacture of manganese by electrolytic processes; more specifically to the purification of the solutions from which the manganese is deposited by electrolysis. Claim No. 27 of plaintiff's application is representative:

Claim 27. A process for producing a purified manganese sulfate solution amenable to electrodeposition of the manganese content thereof, which comprises subjecting a manganese sulfate solution to a preliminary purification treat-

ment which removes substantially all iron and heavy metal impurities, said preliminary purification treatment including treatment with a soluble sulfide, thereafter treating said purified solution maintained at a pH between 7 and 8 with a soluble sulfate of iron which precipitates as a hydrate, said soluble sulfate of iron being used in amount to give about 0.1 gram per liter to 1.0 gram per liter of iron, and recovering a purified solution from the treatment mixture.

In the manufacture of manganese by electrolysis the ore is first subjected to a reducing roast and the roasted
161 ore is then leached. The leached solution contains manganese sulphate with the addition of ammonia sulphate and impurities such as the sulphate of iron, arsenic, copper and other metals. This solution is then purified further by removing iron and arsenic by oxidation. Thereafter it is treated with hydrogen sulphide to convert any metal impurities contained in the sulphides. These sulphides are relatively insoluble and are precipitated. These steps of the process are conceded by the plaintiff to be old in the art as shown by the Hannay et al Patent No. 2,259,418. Further step in the invention is the purification of this solution by adding ferrous sulphate by some other metallic salt which, according to the plaintiff, effects the removal of any remaining copper, nickel, cobalt and other sulphides and sulphide ions from the solution. This last step is the step which the plaintiff claims constitutes an invention, that is, the addition of ferrous sulphate to the solution *after* it has been treated with soluble sulphides. The plaintiff claims that this sequence of steps is critical and that if the ferrous sulphate is added to the solution before the conversion to sulphides the object of the invention cannot be accomplished.

The present position of the plaintiff as to the nature of the impurities remaining before that last step differs from the claims in the specification. In the specification the inventors state:

"...we have been unable to identify even qualitatively the impurities removed in the iron purification or treatment step. Spectrographic analysis has failed to identify the impurities removed

The tendency of metal sulphides to form colloids is well known and free sulphur may be postulated as present in the solutions. It is possible that the function of the treatment step which we employ may be the removal of such solids, probably in the form of microscopic particles."

The question in this case is whether it was old in the art to precipitate impurities such as those listed above or colloidal matters by the use of iron or similar sulphates or whether such a result would be obvious to any one skilled in the art.

162 The defendant claims that the purpose of this last step of adding ferrous sulphate to the solution was to remove any remaining arsenic or colloids; the plaintiff that the purpose was to remove impurities such as copper, nickel, cobalt, etc., and the addition of the ferrous sulphate prior to the conversion into sulphides would not carry out the object of the invention. As said above, however, the plaintiff's present contention is different from that in the application. It would seem that it would be obvious to one "skilled in the art" to add the ferrous sulphate to the solution to purify it of any remaining particles of arsenic or colloids. I agree with the Examiner and the Board of Appeals of the Patent Office in this. It is true that evidence was introduced at the trial to the effect that this final step of purification produced a purer solution of the metallic salt and that is a decided improvement from a commercial standpoint, but commercial success alone is not sufficient to constitute invention.

I agree, therefore, with the defendant that the claims of the plaintiff should be denied.

JENNINGS BAILEY, *Judge*.

* * * * *

Findings of Fact.

1. This is an action under R. S. 4915 (U. S. C., title 35, Sec. 63) in which the plaintiff, Vanadium Corporation of America, sought to have the court authorize the allowance of claims 22, 26, 27, and 28 of application for patent Serial No. 430,258, the plaintiff being the owner of the application by assignment from the applicants, Frank W. Woodman and Miles B. Royer, subject to a royalty-free license to the United States Government.

2. The application in issue relates to a process of purifying manganese sulphate solution in preparation for electrolytic deposition of metallic manganese. According to the application disclosure, conventional purifying processes involve treating the manganese sulphate solution to remove iron and arsenic by oxidation or by the addition of ferrous sulphate, and then treating the solution with a soluble sulphide to convert any metallic impurities to insoluble sulphides, which precipitate. To this known procedure, the applicants add a further step which comprises
164 adding to the manganese sulphate solution a small amount of a soluble metal compound, such as ferrous sulphate, which, it is stated, is converted into a hydroxide which removes residual impurities which otherwise would interfere with the electrodeposition process.

The application states that while the applicants were unable to identify the nature of the impurities removed, it was known that metal sulphides tend to form colloids and that the possible function of the treatment was to remove the sulphides and free sulphur in the form of microscopic solids.

3. It is stated in the application specification that there are many instances in the technical literature where solids have been absorbed by iron hydroxides and traces of colloidal impurities have been removed by such treatment.

4. The Hannay et al. patent No. 2,259,418 discloses a process for purifying manganese sulphate solution includ-

ing the standard methods of removing iron followed by a hydrogen sulphide treatment to precipitate other metallic impurities.

5. The Bureau of Mines Report of Investigations No. 3406 describes various treatments which may be employed to eliminate certain specified impurities from a manganese sulphate solution. In connection with the removal of arsenic, the Report suggests the addition of a small amount of ferrous sulphate to the impure leach solution, if sufficient iron is not already present to effect the purification.

165 One portion of the Bureau of Mines Report No. 3406 states that after the removal of arsenic, the solution is further treated with a soluble sulphide, such as xanthate to precipitate cobalt and nickel.

6. "Quantitative Chemical Analysis" by Prescott and Johnson, on pages 114 and 115, states that the hydrogen sulphide will not completely precipitate arsenic from its hydrochloric acid solution if (1) the solution is not completely saturated with hydrogen sulphide; (2) too much hydrochloric acid is present; (3) the solution contains much pentad arsenic.

7. The applicants, at the time their specification was written, were of the opinion that the impurities remaining after the sulphide treatment were, possibly, in the form of colloidal solids.

8. Since, as set forth in the application, the employment of iron compounds to precipitate colloidal impurities was well known, the step of treating a manganese sulphate solution, already purified according to the Hannay et al process, by adding thereto a soluble metal compound to eliminate residual impurities, would be obvious to one skilled in the art and thus, devoid of invention.

9. Claims 22, 26, 27, and 28 do not define invention over Hannay et al. in view of the disclosure of the state of the art in the application.

10. Since it was known that a preliminary treatment with ferrous sulphate or with a soluble sulphide would not

remove all traces of arsenic, the presence of arsenic as one of the residual impurities after such treatments was a possibility which was obvious to those skilled in the art.

166 11. In view of the Bureau of Mines Report. No.

3406 disclosure of the addition of ferrous sulphate to an impure leach solution to eliminate arsenic, the employment of a soluble metal compound after the conventional purifying steps, as disclosed by Hannay et al, in order to eliminate possible traces of arsenic was an obvious expedient and would not amount to invention.

12. Claims 22, 26, 27, and 28 do not define invention over Hannay et al. in view of the Bureau of Mines Report No. 3406.

13. Claims 22, 26, 27, and 28 are unpatentable in view of the prior art.

At the request of the plaintiff, I make the following additional findings:

14. The application states that the final purification by ferrous sulphate may be in part chemical.

15. The applicants, at the time their specification was written, were of the opinion that the impurities remaining after the sulphide treatment were, possibly, in solution in the manganese solution. The specification states that after the sulphide treatment the solution is "free of precipitated impurities."

16. Applicants' specification, on pages 2 and 3, states "The manganese leach solution (whether produced by the use of sulphuric acid or spent electrolyte) usually
167 contains as impurities iron, arsenic, antimony, zinc, cobalt, nickel, copper, and other metals. It is known that the removal of all these impurities from the manganese electrolyte solution is desirable, since very small concentrations of impurities of the type identified will lower or prevent cathodic deposition of manganese."

Conclusions of Law.

1. The plaintiff is not entitled to a patent containing any of claims 22, 26, 27, and 28 of application Serial No. 430,258.

2. The complaint should be dismissed as to all the claims involved.

JENNINGS BAILEY,
Judge.

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Filed Dec 13, 1950

Judgment.

This action came on to be heard at this term and thereupon consideration thereof, it is this 13th day of December, 1950,

ADJUDGED that the complaint be and it is hereby dismissed, with costs against the plaintiff.

JENNINGS BAILEY,
Judge.

(n)

169

Filed Jan 10 1951

Notice of Appeal.

Notice is hereby given this 10th day of January, 1951, that Vanadium Corporation of America hereby appeals to the United States Court of Appeals for the District of Columbia from the judgment of this Court entered on the 13th day of December, 1950 in favor of Defendant against said Plaintiff.

DONALD GARDNER,
Attorney for Plaintiff.

III.

EXHIBITS.

EXCERPTS FROM PLAINTIFF'S EXHIBIT NO. 1.

Specification.

To All Whom It May Concern:

Be It Known, that we, Frank W. Woodman and Miles B. Royer, citizens of the United States and residents of Boulder City, in the County of Clark, and State of Nevada, have invented a new and useful Improvement in Purification of Manganese Salt Solutions of which the following description is a specification.

This invention described herein may be manufactured and used by or for the Government for Governmental purposes, without the payment to us of any royalty thereon.

Our invention relates to the treatment of manganese bearing solutions. More specifically it relates to the purification of manganese solutions to condition them for electrolysis, although the invention appears to have some advantage in the treatment of manganese solutions for the production of manganese compounds intended for medicinal, chemical and related purposes. The invention concerns particularly the treatment of solutions of manganese sulphate, usually containing ammonium sulphate, and will be so described, although the method involved appears to have some value in the treatment of manganese solutions wherein the manganese appears as a salt of an acid other than sulphuric acid, such, for example, as manganese nitrate solutions and manganese chloride solutions.

Manganese sulphate solutions suitable for electrodeposition of manganese are, in general, produced by a leaching operation using either sulphuric acid or spent electrolyte from which all or a part of the manganese has been stripped. Conventionally, manganese sulphate solutions employed for the electrodeposition of metallic manganese also contain ammonium sulphate with or without other ad-

dition reagents. The manganese leach solution (whether produced by the use of sulphuric acid or spent electrolyte) usually contains as impurities iron, arsenic, antimony, zinc, cobalt, nickel, copper, and other metals. It is known that the removal of all of these impurities from the manganese electrolyte solution is desirable, since very small concentrations of impurities of the type identified will lower or prevent cathodic deposition of manganese. Many methods for the purification of such solutions have been proposed and some of them are employed satisfactorily. Some methods for purification are disclosed and generally discussed in Bureau of Mines Report of Investigation No. 3406 and in United States Patents Nos. 2,119,560 and 2,169,540. In addition to the disclosures made in the publications identified hereinabove, activated charcoal has also been employed. Soluble sulphide compounds have been utilized to advantage. Our present invention, in general, is not intended to take the place of other purification procedures but may be employed as an additional procedure, usually, and preferably, as the final step in the preparation of the electrolyte before delivering it to the cells.

In accordance with our invention, we introduce a relatively small proportion of a metal compound, such as ferrous sulphate, which will precipitate or flocculate as the hydrate, allow the solution to stand and remove the precipitate or floc which forms on standing by suitable means such as filtration. Certain precautions must be taken with respect to pH control, and, depending upon the character of the solution and the type of metal compound employed, other details of control are desired. These matters, however, will be pointed out hereinbelow following the disclosure of one specific method for practicing the invention.

In accordance with one procedure found to be very satisfactory, the impure manganese solution, from the neutralization leach, is classified according to the iron content thereof. When the iron concentration is found to be relatively high, the solution is oxidized by suitable reagents, ordinarily air. Arsenic and antimony precipitate as iron

compounds and the iron is precipitated, principally as ferric hydroxide, if the pH of the solution is controlled to be above pH 4 or preferably about pH 5. The precipitates are removed from the solution by suitable means such as decanting, centrifuging, filtering or the like. The resulting solution, now relatively low in iron, (or a raw leach solution initially low in iron) is thereupon treated with a soluble sulphide such as ammonium sulphide or hydrogen sulphide (the pH of the solution being preferably above 5) to precipitate impurities such as iron, copper, nickel, cobalt, zinc and others. The precipitated impurities are then removed by suitable means such as by filtering the solution. The resulting solution, free of precipitated impurities, is optionally, although not necessarily, further treated by means of activated charcoal and/or soluble xanthates.

The final substantially pure solution resulting from the treatment by the above outlined series of steps is then treated by the addition thereto of a relatively small proportion, e.g. 2 g/l, of an iron compound, such as ferrous sulphate, the pH of the solution being regulated to be at least 4.5 or preferably above, and suitably between 7 and 8. On standing a relatively short time, a floc of iron compounds, preponderantly hydrates, is precipitated. This floc or precipitate appears to remove traces of harmful impurities which are left in the solution after the usual purification procedure. We have not been able to establish the exact mechanism by which these impurities are removed, nor have we been able to identify even qualitatively the nature of the impurities. We have found repeatedly, however, and after a great number of experiments, that manganese sulphate electrolytes which refuse to yield a satisfactory manganese deposit prior to the treatment in accordance with our invention, would readily deposit manganese on the cathodes after the treatment step of our invention was employed.

We have already pointed out that we have been unable to identify even qualitatively the impurities removed in the

iron purification or treatment step. Spectrographic analysis has failed to identify the impurities removed. There are many instances referred to in the technical literature where solids have been absorbed by iron hydroxides and it appears that traces of impurities may be removed by this mechanism. The purification, however, may be in part chemical. The tendency of metal sulphides to form colloids is well known and free sulphur may be postulated as present in the solutions. It is possible that the function of the treatment step which we employ may be the removal of such solids, probably in the form of microscopic particles. Whatever the mechanism of purification may be, however, there is no question of the advantages of the treatment step in that solutions, from which manganese could not be deposited satisfactorily, were repeatedly made more susceptible to plating after the treatment.

In the practice of our invention we sometimes find it advantageous to oxidize the solution during the iron precipitation step. This may be accomplished by blowing air through the solution, or oxidizing agents such as hydrogen peroxide may be employed. Aeration assists in the precipitation when ferrous compounds are present.

The amount of iron compound used in the purification step of our invention is generally very small. 0.3 of a gram per liter of iron is an ample addition under most circumstances. We do not, however, limit ourselves to any particular amount of added iron as the proportion may be varied extensively within the scope of the invention, taking care, however, that the introduced iron is allowed to precipitate before the solution is fed to the electrolyte cell. Our treatment with iron is not to be confused with the removal of iron from the manganese solutions as one conventional purification step heretofore known in the art. Our invention embodies the studied addition of iron compounds as an additional and/or final purification step for manganese solutions to condition the solution for the electrodeposition of manganese of high purity. While prefer-

ably the process of our invention is carried out as the final step, suitably controlled it may be employed in other ways as, for example, in connection with the purification with charcoal or the purification with xanthates. If iron is present in the leach solution, our invention is employed after this iron has been removed substantially entirely by previous purification procedures.

While we ordinarily employ ferrous sulphate which may be readily produced from scrap iron and sulphuric acid, we may use ferric sulphate, ferrous ammonium sulphate or, more generally, ferric and/or ferrous salts, the anions of which preferably are the same as those associated with the manganese in solution. As an example of the practice of our invention, we give below the chemical analysis of four solutions, each of which refused to yield electro-deposited manganese prior to the treatment of our invention but each of which after treatment was satisfactorily employed in the production of manganese electrolytically. In each instance one-tenth of a gram of iron per liter was introduced for purification, the iron being introduced in the form of ferric ammonium sulphate.

TABLE 1—ANALYSIS BEFORE TREATMENT

Test	1	2	3	4
Grams per Liter Mn	28.3	28.6	29.7	27.5
Grams per Liter Fe	0.0001	0.0001	0.0001	0.0001
Grams per Liter As	0.00001	0.00005	0.00005	0.00005
Grams per Liter Co	0.0005	0.0005	0.0005	0.0005
Grams per Liter Ni	0.0005	0.0005	0.0005	0.0002
Grams per Liter Cu	0.0005	0.0005	0.0005	0.0002
Grams per Liter $(\text{NH}_4)_2\text{SO}_4$	176	201	158	128
pH	7.9	8.0	8.0	7.94

TABLE 2—ANALYSIS AFTER TREATMENT

Test	1	2	3	4
Grams per Liter Mn	28.0	26.7	27.9	27.3
Grams per Liter $(\text{NH}_4)_2\text{SO}_4$	174	196	149	125
Grams per Liter As (less than)	0.00001	0.00005	0.00005	0.00005
Grams per Liter Fe (less than)	0.0001	0.0001	0.0001	0.0001
Grams per Liter Co (less than)	0.0001	0.0005	0.0005	0.0005
Grams per Liter Ni (less than)	0.0002	0.0005	0.0002	0.0002
Grams per Liter Cu (less than)	0.0005	0.0002	0.0002	0.0002
pH	7.8	8.0	8.0	8.0

The solutions numbered 1 to 4, inclusive, purified in accordance with our invention and showing the analysis of table 2 were employed in cells over a period of forty-eight hours and periodic inspections made to determine current efficiency, current density at the cathode and voltage, representing an average over the forty-eight hour test. The data obtained is shown in table 3, immediately hereinbelow:

TABLE 3—ELECTRODEPOSITION DATA

Test	1	2	3	4
Current Efficiency, per cent	54.20	51.95	55.51	63.06
Current Density, amps/sq. ft.	20.87	20.87	20.87	21.57
Voltage	4.0	4.0	3.91	4.01

As already pointed out, the amount of iron employed in the purification procedure of our invention may vary. As a general rule, it is not essential that more than approximately 0.3 g/l up to 0.5 g/l be employed, in each instance the calculation being based upon the iron in the compound employed, and generally speaking, we employ less than one gram per liter under all usual conditions which will be encountered. A solution which has been thoroughly purified in accordance with known procedures in general will respond to treatment if 0.1 gram per liter of a soluble iron compound is employed. While our invention is particularly applicable to the treatment of manganese sulphate solutions preparatory to electrodeposition of manganese, it may be employed to purify other manganese solutions such as manganese chloride or manganese nitrate solutions, including solutions from which manganese compounds are to be produced for chemical and like uses.

The invention has been described in detail with specific reference to the use of iron compounds, but, as already indicated, metals other than iron may be used which will form precipitates or flocs under the conditions encountered, such as aluminum, beryllium, titanium and the like. As in the case of iron, the pH must be properly controlled to produce the hydrate precipitate, and the proportions used are also small, generally of the order discussed for iron. While, on

the basis of our present knowledge, the use of iron is preferred, we have also obtained very good results with aluminum. While iron is the more readily available, and the price is low, its continuous use will probably be indicated. We do not wish to be limited in the scope of our invention, however, except within the definition of the appended claims.

What we claim as new and desire to protect by Letters Patent of the United States is:

1. In the treatment of a manganese bearing solution as part of a purification procedure, the steps of introducing into the solution a relatively small proportion of an iron compound, causing the iron compound so introduced to precipitate and removing the resulting precipitate.

2. The method defined in claim 1 wherein the iron compound introduced is a salt having an anion the same as that associated with the manganese in solution.

3. In the treatment of a manganese bearing solution preparatory to electrolyzing the same for the production of manganese, the steps of subjecting the solution to a purification procedure designed to remove all metallic impurities present followed by the step of introducing into the substantially purified solution a relatively small proportion of an iron compound, and removing the precipitate formed as a result of the introduction of such iron compound.

4. The method of purifying a manganese sulphate solution which includes the step of introducing into the manganese sulphate solution a relatively small proportion of an iron compound of the class consisting of ferric and ferrous salts of sulphuric acid.

5. The method of purifying a manganese sulphate solution which includes the step of introducing into the manganese sulphate solution ferrous ammonium sulphate.

6. The method of conditioning a manganese sulphate solution preparatory to the production of electrolytic manganese therefrom which comprises subjecting the solution

to a purification procedure to remove therefrom metals occurring in the solution as impurities, thereafter introducing into the substantially purified solution a relatively small proportion of an iron compound of the class consisting of ferric and ferrous salts of sulphuric acid and then removing the resulting precipitate.

7. In the treatment of manganese bearing solutions as a part of a purification procedure, the steps of introducing a relatively small proportion of a metal compound capable of conversion to an insoluble hydrate under the conditions found in the solution, adjusting the pH of the solution to cause the hydrate to precipitate, and removing the precipitate.

8. In the treatment of a manganese sulphate solution for the purpose described, the steps of introducing a relatively small proportion of an iron compound, adjusting the pH to precipitate iron in combined form, and removing the resulting precipitate.

DEPARTMENT OF COMMERCE
UNITED STATES PATENT OFFICE
WASHINGTON 25, D. C.

BEFORE THE BOARD OF APPEALS ON APPEAL No. 14,259

In re application of:

Frank W. Woodman et al.

Serial No. 430,258

Filed February 10, 1942

For Purification of Manganese Salt Solutions

Examiner's Statement.

This is an appeal from the final rejection of claims 14-19 and 21-25 inclusive. All but claim 22 have been cancelled and new claims 26, 27, and 28 substituted therefore for purpose of appeal, so this statement is accordingly forwarded with the reasons for rejection of claims 22, 26, 27, and 28, all of the claims now in the case.

In view of the entry of the amendment after final rejection, new grounds for rejection made necessary by the new claims will not be considered as reopening prosecution before the primary examiner.

The rejected claims:

Claim 22. A process for producing a purified manganese salt solution amenable to electrodeposition of the manganese content thereof, which comprises subjecting a manganese salt solution to a preliminary purification treatment which removes substantially all iron and heavy metal impurities, said preliminary purification treatment including treatment with a soluble sulfide, thereafter treating said purified solution maintained at a pH of at least 4.5 with a soluble compound of a metal selected from the group consisting of iron, aluminum, beryllium and titanium which precipitates as a hydrate, said soluble compound being used in amount to give about 0.1 gram per liter to 1.0 gram per liter of metal of said group, and recovering a purified solution from the treatment mixture.

Claim 26. A process for producing a purified manganese sulfate solution amenable to electrodeposition of the manganese content thereof, which comprises subjecting a manganese sulfate solution to a preliminary purification treatment which removes substantially all iron and heavy metal impurities, said preliminary purification treatment including treatment with a soluble sulfide, thereafter treating said purified solution maintained at a pH between 7 and 8 with a soluble compound of a metal selected from the group consisting of iron, aluminum, beryllium and titanium which precipitates as a hydrate, said soluble compound being used in amount to give about 0.1 gram per liter to 1.0 gram per liter of metal of said group, and recovering a purified solution from the treatment mixture.

Claim 27. A process for producing a purified manganese sulfate solution amenable to electrodeposition of the manganese content thereof, which comprises subjecting a manganese sulfate solution to a preliminary purification treatment which removes substantially all iron and heavy metal impurities, said preliminary purification treatment including treatment with a soluble sulfide, thereafter treating said purified solution maintained at a pH between 7 and 8 with a soluble sulfate of iron which precipitates as a hydrate, said soluble sulfate of iron being used in amount to give about 0.1 gram per liter to 1.0 gram per liter of iron, and recovering a purified solution from the treatment mixture.

Claim 28. A process for producing a purified manganese sulfate solution amenable to electrodeposition of the manganese content thereof, which comprises subjecting a manganese sulfate solution to a preliminary purification treatment which removes substantially all iron and heavy metal impurities so that the solution contains not over about 0.0001 gram per liter of iron, said preliminary purification treatment including treatment with a soluble sulphide, thereafter treating said purified solution maintained at a pH between 7 and 8 with a soluble compound of a metal

selected from the group consisting of iron, aluminum, beryllium and titanium which precipitates as a hydrate, said soluble compound being used in amount to give about 0.1 gram per liter to 1.0 gram per liter of metal of said group, and recovering a purified solution from the treatment mixture.

The references relied upon:

Hannay	2,259,418	Oct. 14, 1941
Jacobson	1,137,005	Apr. 27, 1915

Bureau of Mines Report of Investigations, No. 3406, pages 6, 7, and 8.

Now cited:

Prescott and Johnson, Qualitative Chemical Analysis, 5th Edition, pages 114 and 115. Published by D. VanNostrand Co., N. Y., (1901). Copy in Division 59.

THE CONTENTED INVENTION

The contended invention is a process for purifying manganese salt solutions. The electrolysis of such solutions to deposit manganese requires high purity. Applicant's process involves a preliminary treatment which includes addition of a soluble sulfide to remove heavy metals, followed by addition of a salt of one of the metals of the group consisting of iron, aluminum, beryllium, and titanium in an amount which gives from 0.1 to 1.0 gram per liter of the metal ion in solution, at a pH at which the metal salt hydrolyzes to the hydroxide.

Applicant states that the precipitation of heavy metals as sulfides leaves colloidal matter in suspension in the solution, and that this is flocculated and removed by the metal hydroxide with precipitates by hydrolysis.

Applicant also states that the preliminary treatment removes all iron, and that if necessary the solution is subjected to oxidation to effect this. However, the claims merely broadly state that iron and other heavy metals are removed by a preliminary treatment including treatment

with a soluble sulfide and omit any other procedure which might remove iron.

THE REFERENCES

Hannay shows the process of extracting manganese from its ore as a salt, purifying the salt, and electrolyzing it to manganese metal. The purification is stated to be by precipitation of metal impurities with hydrogen sulfide after removal of iron from the solution.

The cited portion of the Bureau of Mines report deals with the purification of manganese salt solutions to prepare them for electrolysis. The publication teaches adding an iron salt to a leach solution at a pH of 7. The purpose is to precipitate arsenic, by adsorption on the iron hydroxide.

The Jacobson patent shows the addition of aluminum and iron sulfate to water to clarify it. The sulfates hydrolyze, forming aluminum and iron hydroxide precipitates, which carry out of the water any colloidal matter present.

The Prescott and Johnson text is cited merely to show that arsenic is not invariably precipitated by H_2S . Note 10 shows that it must be in a particular valence state, and that the hydrogen ion concentration has a marked effect on the extent of precipitation when the arsenic is in the correct valence state.

THE REJECTION

The claims are all rejected as being unpatentable over Hannay taken with the Bureau of Mines Report or Jacobson.

There would be no invention in further treating a solution, which has been treated with hydrogen sulfide under conditions to precipitate heavy metals, to precipitate arsenic as is taught by the Bureau of Mines bulletin. Arsenic would not necessarily be removed by hydrogen sulfide treatment; whether it would or not would depend upon pH and other conditions when H_2S is added. See paragraph

10 of Prescott and Johnson cited above. The art would therefore be entitled to append the Bureau of Mines iron precipitation to the Hannay sulfide treatment for the purpose which the Bureau of mines discloses it.

Applicant urges that the addition of iron is for a different purpose, however. In the sulfide treatment of Hannay, colloidal sulfur or sulfides may remain in the solution and interfere with the subsequent electrolytic separation of manganese. Applicant adds the iron or other salt in order to form a flocculent precipitate of iron hydroxide which carries down with it the colloidal matter. Use of iron and aluminum salts is old for removal of colloidal matter from water, as shown by Jacobson, and it would not amount to invention to use this way to clarify a manganese sulfate solution.

Applicants have argued that the claims call for addition of iron salt to an iron-free solution whereas the Bureau of Mines report shows adding iron sulfate to a solution which already contains some iron. It is not apparent why this should make any difference. The report adds sufficient iron salt to bring the resulting iron content within the range specified by applicants. It seems obvious that if none were initially present, more would have to be added.

For the reasons stated, rejection of the claims is submitted to be proper.

Respectfully submitted,

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IN THE UNITED STATES PATENT OFFICE
BEFORE THE BOARD OF APPEALS

APPEAL No. 14,259

In re application of
Frank W. Woodman et al
Serial No. 430,258

Filed February 10, 1942

For Purification of Manganese Salt Solutions

Brief for Applicants

The appealed claims are as follows:

22. A process for producing a purified manganese salt solution amenable to electrodeposition of the manganese content thereof, which comprises subjecting a manganese salt solution to a preliminary purification treatment which removes substantially all iron and heavy metal impurities, said preliminary purification treatment including treatment with a soluble sulfide, thereafter treating said purified solution maintained at a pH of at least 4.5 with a soluble compound of a metal selected from the group consisting of iron, aluminum, beryllium and titanium which precipitates as a hydrate, said soluble compound being used in amount to give about 0.1 gram per liter to 1.0 gram per liter of metal of said group, and recovering a purified solution from the treatment mixture.

26. A process for producing a purified manganese sulfate solution amenable to electrodeposition of the manganese content thereof, which comprises subjecting a manganese sulfate solution to a preliminary purification treatment which removes substantially all iron and heavy metal impurities, said preliminary purification treatment including treatment with a soluble sulfide, thereafter treating said purified solution maintained at a pH between 7 and 8 with a soluble compound of a metal selected from the group consisting of iron, aluminum, beryllium and titanium which precipitates as a hydrate, said soluble compound being used in amount to give about 0.1 gram per liter to 1.0 gram

per liter of metal of said group, and recovering a purified solution from the treatment mixture.

27. A process for producing a purified manganese sulfate solution amenable to electrodeposition of the manganese content thereof, which comprises subjecting a manganese sulfate solution to a preliminary purification treatment which removes substantially all iron and heavy metal impurities, said preliminary purification treatment including treatment with a soluble sulfide, thereafter treating said purified solution maintained at a pH between 7 and 8 with a soluble sulfate of iron which precipitates as a hydrate, said soluble sulfate of iron being used in amount to give about 0.1 gram per liter to 1.0 gram per liter of iron, and recovering a purified solution from the treatment mixture.

28. A process for producing a purified manganese sulfate solution amenable to electrodeposition of the manganese content thereof, which comprises subjecting a manganese sulfate solution to a preliminary purification treatment which removes substantially all iron and heavy metal impurities so that the solution contains not over about 0.0001 gram per liter of iron, said preliminary purification treatment including treatment with a soluble sulphide, thereafter treating said purified solution maintained at a pH between 7 and 8 with a soluble compound of a metal selected from the group consisting of iron, aluminum, beryllium and titanium which precipitates as a hydrate, said soluble compound being used in amount to give about 0.1 gram per liter to 1.0 gram per liter of metal of said group, and recovering a purified solution from the treatment mixture.

The references relied upon are:

Hannay	2,259,418	Oct. 14, 1941
Jacobson	1,137,005	Apr. 27, 1915

Bureau of Mines Report of Investigations, No. 3406,
pages 6, 7, and 8.

The Examiner in the Examiner's Statement also has cited:

Prescott and Johnson, Qualitative Chemical Analysis, 5th Edition, pages 114 and 115. Published by D. Van-Nostrand Co., N. Y., (1901). Copy in Division 59.

APPLICANTS' INVENTION

The invention relates to a process for producing a purified manganese salt solution which is amenable to electro-deposition of the manganese content thereof. The electrolysis of such solutions to deposit manganese requires high purity. Applicants found that manganese salt solutions which had been purified by known methods but which still refused to yield electrodeposited manganese could be treated to purify them according to the present invention and that after such treatment they could be employed satisfactorily in the production of electrodeposited manganese. It is emphasized throughout applicants' specification that their treatment is a final treatment which is applied to the solution after other known methods of treatment have been resorted to and that applicants' final treating step is performed on a manganese solution which is *substantially free from all iron and heavy metal impurities such as arsenic, antimony, zinc, cobalt, nickel and copper.*

In applicants' process the manganese solution is first subjected to a preliminary purification treatment which removes substantially all iron and heavy metal impurities. This preliminary purification includes as one of its steps, treatment of the solution with a soluble sulfide, as for example hydrogen sulfide or ammonium sulfide. After the preliminary treatment which includes the employment of a soluble sulfide has been carried out and the solution is *substantially free from all iron and heavy metal impurities*, the solution is given a final treatment at a pH of at least 4.5 by the addition of iron sulfate or, stated more broadly, with a soluble compound of a metal selected from the group consisting of iron, aluminum, beryllium and titanium,

which precipitates as a hydrate. The soluble compound is used in amount to give about 0.1 gram per liter to 1.0 gram per liter of iron or other metal employed.

One procedure for purifying a manganese solution so as to make it suitable for the electrodeposition of manganese is described in applicants' specification (page 4, line 1, to page 5, line 11). This procedure involves the five following steps:

(1) If the iron concentration of the manganese solution obtained by leaching an ore is high, the solution is oxidized with air while the pH of the solution is maintained above 4 or 5. This precipitates the bulk of the iron and also precipitates arsenic and antimony.

(2) The precipitate is removed from the solution.

(3) The solution is treated with hydrogen sulfide or ammonium sulfide, the pH of the solution being maintained above 5. This precipitates substantially all of the iron, copper, cobalt, nickel, zinc and other impurities.

(4) The precipitate is removed, leaving a solution containing only traces of iron, arsenic, cobalt, nickel and copper as for example in the amounts shown in Table 1 on page 7.

(5) The manganese solution from which substantially all of the iron and other impurities have been removed is then treated with ferrous sulfate, the solution being maintained at a pH of at least 4.5 and preferably between 7 and 8. The solution is allowed to stand, whereon iron hydroxide precipitates and carries down with it the remaining traces of impurities.

Applicants' invention resides in the combination of step 5 with a preliminary purification treatment which removes substantially all iron and heavy metal impurities, the preliminary purification step including as one of its features the employment of a soluble sulfide. Steps 1 through 4 of the above referred to procedure are not set forth in detail in the claims because the net effect of these four steps is to produce a manganese sulfate solution from which substantially all of the iron and heavy metal impurities have been

removed so that the solution is a substantially pure solution. Applicants' invention resides in treating a solution which contains only traces of impurities, at a pH of at least 4.5 and preferably between 7 and 8 with ferrous sulfate or its equivalent. Thus on page 6 of the specification it is stated:

"If iron is present in the leach solution, our invention is employed after this iron has been removed substantially entirely by previous purification procedures."

Table 1 on page 7 gives analyses of four solutions which are treated according to the invention. It can be seen from this table that applicants' final purification treatment with ferrous sulfate (step 5 above) is not for the purpose of removing iron because the solution before treatment contains only 0.0001 gram per liter of iron. The solutions given in Table 1, even though they were substantially free from all impurities, refused to yield electrodeposited manganese, but after treatment according to step 5 above with iron sulfate, satisfactorily electrodeposited manganese.

THE REFERENCES

Hannay et al. patent 2,259,418 discloses a process of extracting manganese from its ore as a salt, purifying the salt and electrolyzing it to manganese metal. In carrying out the purification step the iron is first removed by standard methods and thereafter the solution is treated with hydrogen sulfide to precipitate impurities such as nickel, cobalt, zinc, lead, arsenic and antimony.

The cited portion of the Bureau of Mines Report deals with the purification of manganese salt solutions to prepare them for electrolysis. The publication teaches adding an iron salt and an oxidizing agent (manganese dioxide) to an *impure* leach solution which has not been subjected to a preliminary purification and contains .056 gram per liter of iron. The purpose is to precipitate iron as iron hydroxide and also to remove arsenic by adsorption on the iron hydroxide. The Examiner at first cited only pages 6 and 7 of the Bureau of Mines Report but has now included

page 8. Page 9 should also be included to complete this disclosure. A copy of page 9 is filed herewith. On pages 8 and 9 of the Report it is stated:

“A Purification Batch

“Referring to a typical purification batch, analysis given above: Iron to the extent of 0.05 gram per liter as ferrous sulphate was dissolved in the batch, then 0.5 gram per liter manganese dioxide from the spent electrolyte was added, and the solution was agitated for 3 hours. The solution was filtered in all-lead, plate-and-frame-type pressure filter press. Analysis of the filtrate showed that iron had dropped to 0.25 mg per liter and arsenic to less than 0.05 mg per liter. The solution from the filter flowed into a second lead-lined tank and was treated with a mixture of 0.3 gram per liter of sodium ethyl xanthate and 0.2 gram per liter of potassium pentasol xanthate. The solution was stirred by hand to obtain complete dissolution of the reagents, and 6 hours was allowed for complete reaction of the xanthate to precipitate cobalt and nickel. The solution was filtered in an all-lead, plate- and frame-type pressure filter press and pumped into a catholyte feed storage tank, lead-lined, and of 800 liters capacity. Nickel and cobalt concentrations of the catholyte feed were less than 1 mg per liter, respectively.”

The Jacobson patent 1,137,005 shows the addition of aluminum and iron sulfate to water to clarify it. The sulfates hydrolyze, forming aluminum and iron hydroxide precipitates, which carry out of the water any colloidal matter present.

The Prescott and Johnson text is cited merely to show that arsenic is not invariably precipitated by H_2S .

ARGUMENT

The claims were rejected as being unpatentable over Hanay taken with the Bureau of Mines Report or Jacobson. The Examiner has held that there would be no invention in *further* treating a solution, which has been treated with

hydrogen sulfide under conditions to precipitate heavy metals, in order to precipitate arsenic, as is taught by the Bureau of Mines Report.

There is no teaching in either Hannay or the Bureau of Mines Report of combining the two processes and there certainly is no teaching of combining the two processes in such manner that the Hannay process is first employed and then the Bureau of Mines process is employed as a final step. It is to be noted particularly, as stated on page 7 of the Bureau of Mines Report, that the ferrous sulfate was added to the *impure* leach solution containing .056 gram per liter of iron. The solution to which the ferrous sulfate was added is the impure solution given in the table at the bottom of page 6 which contains all of the impurities resulting from leaching the manganese ore. It contains as impurities iron, arsenic, copper, nickel, cobalt and lead.

The actual process employed according to the Bureau of Mines Report is described on pages 8 and 9 of the report which have been quoted herein. Iron to the extent of 0.05 gram per liter as ferrous sulfate was dissolved in the *impure* leach solution, the composition of which is given in the table at the bottom of page 6, and then 0.5 gram per liter manganese dioxide from the spent electrolyte was added and the solution was agitated for 3 hours. The manganese dioxide was added for the purpose of oxidizing the ferrous iron to ferric iron. Reference is made to such oxidation on page 7, wherein it is stated: "Oxidation of the remaining ferrous iron with air or, more conveniently, with manganese dioxide anode slime leads to iron precipitation, as shown in the procedure." The addition of the ferrous sulfate reduced the iron in solution from .056 gram per liter to .025 gram per liter, and also lowered the arsenic from 0.2 mg per liter to less than 0.05 mg per liter. The treatment with ferrous sulfate to remove iron and arsenic was followed by a treatment with xanthate to remove cobalt and nickel. It is thus seen that the Bureau of Mines process involves first adding ferrous sulfate to an *impure* leach solution containing a large amount of iron, and there-

after treating the solution with xanthate to remove cobalt and nickel. The manganese solution to which the ferrous sulfate is added contained .056 gram per liter of iron, which is 560 times the amount of iron contained in applicants' solution as given in Table 1 on page 7.

Hannay discloses first removing iron and then removing impurities such as nickel, cobalt, zinc, lead, arsenic and antimony by treatment with hydrogen sulfide. The Bureau of Mines Report teaches first removing iron by adding ferrous sulfate and thereafter removing cobalt and nickel by employing xanthates. In each process the first step is to remove iron by treating the impure leach solution. If there is any obvious combination of the two processes it would be to remove iron by the addition of ferrous sulfate and then follow this treatment with a hydrogen sulfide treatment for the removal of cobalt and nickel instead of employing the xanthate treatment of the Bureau of Mines Report. There certainly is no suggestion in either of the references to add ferrous sulphate to a solution from which substantially all iron and heavy metal impurities have been removed previously by a preliminary purification treatment. Hannay teaches that arsenic, nickel and cobalt are removed by the hydrogen sulfide treatment. Since the purpose of adding ferrous sulfate according to the Bureau of Mines Report is to remove arsenic, it would not be obvious to add ferrous sulfate to a solution from which the arsenic had already been removed by employing hydrogen sulfide. Furthermore, the Bureau of Mines process reduces arsenic only to less than 0.05 mg per liter so that it would not be obvious for applicants, or any one else skilled in the art, to add ferrous sulfate to a manganese solution which had already been purified to such an extent that it contained only 0.01 mg per liter arsenic as shown in Table 1 of applicants' specification.

Neither Hannay nor the Bureau of Mines Report teaches that there is any particular virtue in employing a treatment with hydrogen sulfide and then following with a treatment with ferrous sulfate. That is the combination covered by the appealed claims.

The solutions described in Table 1 on page 7 of applicants' specification were obtained by oxidizing the solution with air to convert the ferrous iron to ferric iron, then removing the precipitated iron, thereafter treating the solution with hydrogen sulfide and removing the precipitated impurities. In other words, the substantially pure solution referred to in Table 1 was obtained according to the process of the Hannay patent. However, those solutions refused to yield electrodeposited manganese. Applicants made the discovery that they could be made to yield electrodeposited manganese by further treating them with iron in the form of ferric ammonium sulfate. Since the solutions of Table 1 were already substantially pure solutions (as contrasted with the impure solution of the Bureau of Mines Report), there was no incentive for applicants to apply any further treatment to the solutions. However, they made the attempt and were rewarded by discovering that it made the solutions capable of electrodepositing manganese. The addition of ferrous sulfate to an impure leach solution containing .056 gram per liter of iron in order to reduce the iron to .025 gram per liter of iron (see page 8 of the Bureau of Mines Report) is an entirely different thing from adding ferrous sulfate to a previously purified solution which contains only .0001 gram per liter of iron. One would not ordinarily think that any useful purpose would be served by adding ferrous sulfate to a solution which already was so pure that it contained only .0001 gram per liter of iron.

The combination of Hannay with Jacobson is not believed to be at all pertinent since Jacobson relates merely to the purification of water and not to the purification of a manganese salt solution.

It is submitted that the claims clearly and patentably distinguish over the references taken singly and also patentably distinguish from any legitimate combination of the references, and that the claims should be allowed.

Respectfully submitted,

STEBBINS, BLENKO & WEBB,
Attorneys for Applicants.

February 6, 1948.

DEPARTMENT OF COMMERCE
UNITED STATES PATENT OFFICE
WASHINGTON 25, D. C.

BEFORE THE BOARD OF APPEALS

In re application of:
Frank W. Woodman et al
Ser. No.: 430,258
Filed: Feb. 10, 1942
For: Purification Of Manganese
Salt Solutions

Examiner's Reply Under Rule 137.

Two grounds of rejection have been used and the brief is directed mainly only to one of them.

The only comment applicants make regarding the rejection on Hannay taken with Jacobson is the next to the last paragraph on page 11 of the brief. The examiner's position on this is that any process for clarification of water is obviously equally applicable to clarification of solutions. That the problem may be one of removing colloidal matter is indicated by applicants' specification, page 5, last paragraph.

The main part of the brief is taken up with a discussion of the rejection on the ground that it requires no invention to remove any arsenic remaining after treatment with H_2S as in Hannay, by the method shown by the Bureau of Mines report to remove arsenic.

The brief introduces reference to page 9 of the Bureau of Mines report. The examiner has no objection its consideration by the Board, but it is not deemed relevant to any issue raised on this appeal. The general disclosure of adding ferrous sulfate and oxidizing at pH 7 to remove arsenic is not affected or restricted any by such further treatment as may have been carried out by the authors to remove other materials.

The argument on page 9 of the brief side-steps the issue on this ground of rejection. Hannay shows H_2S precipitation of impurities. The Prescott and Johnson text is cited to show that, to a chemist, it would readily appear that H_2S

would not necessarily remove all arsenic. It would not require invention to remove any remaining arsenic by adding a ferrous salt, oxidizing, and hydrolyzing at pH 7 to precipitate the iron and arsenic as taught by the Bureau of Mines report. The claims read on such an obvious procedure. There is no mechanistic concept in this rejection of substituting specific element X of A for that shown by B in an old combination, as applicants appear to believe is necessary in order to combine references.

On page 10 the brief applicants argue that there would be no point in view of the art cited in treating a solution containing less than 0.01 mg. per liter of arsenic in order to remove arsenic. The argument is irrelevant since not one of the rejected claims specifies how much arsenic is in the solution treated. Applicants refer to the specification as showing such a value, but the figures set out in the specification are given by way of example only and the last three lines of the specification state that applicants do not wish to be limited except by the definition in the claims.

Page 10 of the brief again raises the point that the Bureau of Mines report mentions reduction of arsenic to less than 0.05 mg. per liter. This final figure is higher than that with which applicants argue that they start. However, aside from the fact that the claims do not specify any value, it must be pointed out that the figure given by the publication is an upper limit. Applicants are not justified in inferring that there must be as much as 0.05 mg. per liter of arsenic present where the reference says less than 0.05 mg.; the actual value may be much less than this and if the prior workers used a test sensitive only to the extent of 0.05 mg. per liter, they could ethically report only that the arsenic is below this figure even though in fact no arsenic at all remained. Moreover, no reason is seen why a treatment which removes a portion of arsenic when a substantial amount is present, should not also be expected remove some arsenic when only a lesser amount is initially present.

Respectfully submitted,

P. W. SHEPARD,
Examiner, Division 59.

R.L.C.

Decision of the Board of Appeals.

Appeal No. 14,259

LB

Hearing: March 10, 1948

IN THE UNITED STATES PATENT OFFICE
BEFORE THE BOARD OF APPEALS

Ex parte Frank W. Woodman and Miles B. Royer
Application for Patent filed February 10, 1942, Serial
No. 430,258. Purification of Manganese Salt Solutions.
Messrs. Stebbins, Blenko and Webb for applicants.

Appellants had appealed from the final rejection of claims 14 to 19 and 21 to 25, both inclusive. Since filing the appeal, however, they have cancelled all but claim 22 and added new claims 26, 27 and 28. The issue now is with respect to claims 22, 26, 27 and 28. No claims have been allowed.

Claim 22 is representative of the subject matter on appeal and is reproduced herebelow:

22. A process for producing a purified manganese salt solution amenable to electrodeposition of the manganese content thereof, which comprises subjecting a manganese salt solution to a preliminary purification treatment which removes substantially all iron and heavy metal impurities, said preliminary purification treatment including treatment with a soluble sulfide, thereafter treating said purified solution maintained at a pH of at least 4.5 with a soluble compound of a metal selected from the group consisting of iron, aluminum, beryllium and titanium which precipitates as a hydrate, said soluble compound being used in amount to give about 0.1 gram per liter to 1.0 gram per liter of metal of said group, and recovering a purified solution from the treatment mixture.

The references relied upon are:

Jacobson, 1,137,005, Apr. 27, 1915.

Hannay et al, 2,259,418, Oct. 14, 1941.

Bureau of Mines Report of Investigations, No. 3406, pages 6, 7 and 8.

Prescott and Johnson, Qualitative Chemical Analysis, 5th Edition, pages 114 and 115. Published by D. VanNostrand Co., N. Y., (1901).

The appealed subject matter relates to a process for the production of a purified manganese salt solution, particularly a manganese sulphate solution containing ammonium sulphate. In carrying out the process, the manganese ore is calcined and leached. After the iron originally in the calcined and leached ore has been reduced to a negligible amount (.0001 gms. per liter) and other impurities substantially reduced by suitable processes including the addition to the leach of soluble sulphide compounds, appellants add a controlled amount of iron salts to give 0.1 to 1.0 grams per liter of metallic iron in solution at a pH at which the metal salt hydrolyzes to the hydroxide. Appellants state that the manganese salt solution after this treatment will yield a substantially chemically pure manganese salt and will be a solution which will yield to electrodeposition of the manganese where otherwise treated it would not. Appellants are not certain why this solution after the iron dosing is amenable to electrodeposition while allegedly other solutions are not, but speculates that traces of impurities may be removed in part by chemical action and in part by inclusion of microscopic particles or sulphur in the colloids formed in the solution. Appellants contemplate using salts of metals other than iron so long as they are capable of forming flocs or precipitates.

The Bureau of Mines report discloses successful electrodeposition of manganese in which the leached liquor from a manganese ore is treated with an iron salt to precipitate out the major portion of the iron salts and, along with it, arsenic. Prior to passing to the electrolytic cell, xanthates, sulphur dioxide and "Goulac," a sulphite paper by-product, are added to the liquor. It is apparently the Examiner's position that the addition to the leaching liquor of iron, in any amount necessary to effect the precipitation of the iron salts contained in the solution and the arsenic, either during the initial portion of the clarification of the

manganese solution or subsequently to other treatment, is not patentable. Appellants argue that their method effects clarification of the solution to such extent as to permit electrodeposition of the metal with solutions where a single step clarification is not effective. However, the Bureau of Mines report indicates that the method therein described is operative and it should be clear that if initially insufficient iron is present in the solution to effect proper precipitation of impurities, more iron could be added, without invention. We agree with the Examiner that the claims are unpatentable over the publication particularly in view of Hannay et al who on page 2, lines 11 to 15 describes the use of hydrogen sulphide as a means to precipitate out metallic impurities and who, substantially, discloses all of appellants' process except the last step of adding more iron.

Furthermore, appellants' additional step of adding iron as described on page 3, lines 13 to 19 and in line 20, page 6, is only by preference a *final* step. In such a case, the claims state no invention over the "Purification Batch" on page 8 of the Bureau Report where the iron sulphate is first added and the sulphide (Xanthate) treatment is the final step. The result seems to be the same; that is, manganese is successfully deposited and the Bureau Report shows, in general, the same current efficiency as do appellants.

The Examiner has also rejected the claims as unpatentable over Hannay et al in view of Jacobson. The latter patent discloses the purification of drinking water by the addition of a metallic salt to ultimately precipitate out, as a sulphate, metallic iron. We do not believe that the existence of the Jacobson patent teaches tacking on the step therein performed to what is performed in Hannay et al nor is there any suggestion that the processes ought to be combined.

The decision of the Examiner is affirmed.

In event of appeal attention is directed to *In re Boyce*, 32 C.C.P.A. 718; 144 Fed. (2d) 896; 1944 C. D. 609; 568 O.G. 568; 63 U.S.P.Q. 80, in regard to specifically including

in the appeal notice *all* grounds of rejection in the Examiner's Statement not expressly overruled by the Board.

BOARD OF APPEALS

F. J. PORTER,
Examiner-in-Chief.

L. P. McCANN,
Examiner-in-Chief.

MICHAEL HERTZ,
Examiner-in-Chief.
(Acting)

March 26, 1948

Messrs. STEBBINS, BLENKO & WEBB
1319 Farmers Bank Building
Pittsburgh 22, Pennsylvania

IN THE UNITED STATES PATENT OFFICE
BEFORE THE BOARD OF APPEALS

Appeal No. 14,259.

In re application of FRANK W. WOODMAN ET AL Serial No.
430,258 Filed February 10, 1942 For Purification of
Manganese Salt Solutions

Petition for Reconsideration.

We ask reconsideration of the Board of Appeals' decision dated March 26, 1948, the principal grounds of our request being that the Board erred in holding:

1. That results equivalent to applicants' results are obtained according to the Bureau of Mines report.
2. That invention is not involved in adding more iron to the Bureau of Mines process or to the Hannay process.

I

In the purification of a manganese salt solution according to the Woodman et al. process, assuming that the manganese solution contains as impurities iron, arsenic, antimony, copper, cobalt, nickel and zinc, the principal steps are as follows:

1. The solution is oxidized with air. This precipitates the bulk of the iron. Arsenic and antimony also precipitate as iron compounds, but the other impurities such as copper, cobalt, nickel and zinc remain in solution. The precipitate is then filtered from the solution.

2. Ammonium sulphide or hydrogen sulphide is added, thus converting the copper, cobalt, nickel, zinc and remaining iron to the sulphides. A large part of all of these sulphides precipitate and are removed from the solution by filtration. It is believed, however, that traces of these sulphides remain in solution and account for the fact that the solution is not amenable to continuous electrodeposition of manganese. The quantities of impurities remaining in the solution at this stage of the process are so small that it is not possible to determine them with precision.

3. Ferrous sulphate is added to the solution at a pH of at least 4.5. On standing a relatively short time, a floc of iron compounds, preponderantly hydrates, is precipitated. This floc or precipitate is believed to remove the traces of harmful impurities, such as the sulphides of copper, cobalt, nickel and zinc which remained after the sulphide treatment.

The process disclosed in the Bureau of Mines report is as follows:

1. Ferrous sulphate is added to the impure manganese leach solution to precipitate iron and arsenic. This has no effect on the cobalt, nickel or other impurities.

2. The solution is treated with a xanthate. This precipitates cobalt and nickel, which are filtered from the solution.

It is believed that the xanthate treatment leaves traces of cobalt and nickel compounds in the solution, but the Bureau of Mines report teaches nothing with regard to removing these traces of impurities.

The Hannay patent 2,259,418 discloses a process involving the following steps:

1. Iron is removed by "standard methods."

2. Hydrogen sulphide is added to remove impurities such as nickel, cobalt, zinc, lead, iron, arsenic and antimony.

II

The Board of Appeals in its decision agreed with the Examiner's position that the addition to the leaching liquor of iron, in any amount necessary to effect the precipitation of the iron salts contained in the solution and the arsenic, either during the initial portion of the clarification of the manganese solution or subsequently to other treatment, is not patentable. The Board of Appeals decision states "It should be clear that if initially insufficient iron is present in the solution to effect proper precipitation of impurities, more iron could be added, without invention."

A distinction must be drawn between iron added prior to a sulphide treatment and iron added after a sulphide treat-

ment. Iron added before a sulphide treatment is for the purpose of removing iron and arsenic. It does not remove cobalt, nickel or other impurities. The treatment of the solution with hydrogen sulphide converts nickel, cobalt and other metal impurities into the sulphides and causes the largest part of these sulphides to precipitate so that they can be removed. However, traces of these sulphides remain in solution. The addition of iron after a sulphide treatment is not for the purpose of removing iron or arsenic but is for the purpose of removing the sulphides of nickel, cobalt and other metals remaining in solution from the sulphide treatment.

There is no teaching in the Bureau of Mines report or the Hannay patent that iron should be added following a sulphide treatment. According to the Bureau of Mines report, iron is added for the purpose of removing iron and arsenic. This is followed by a xanthate treatment for the removal of nickel and copper. Since at this stage iron, arsenic, cobalt and nickel have been removed, there would be no incentive for adding on another step of adding iron, since the purpose in adding iron initially has already been accomplished.

Similarly, in the Hannay process iron is first removed, then the solution is treated with hydrogen sulphide to remove the remaining iron as well as arsenic, antimony and other impurities. Since the purpose of the Bureau of Mines process in adding iron is to remove iron and arsenic, and since iron and arsenic have already been removed by hydrogen sulphide in the Hannay process, there would be no incentive for anyone to tack on to the Hannay process the additional step of adding further iron.

Referring to the paragraph beginning at the bottom of page 3 of the Board's decision, it is to be noted that each of applicants' claims sets forth a preliminary step including treatment with a soluble sulphide and a subsequent step of adding iron. Irrespective of applicants' disclosure, his

claims are to a preliminary sulphide treatment followed by a subsequent iron treatment. This is the reverse of the order of steps in the Bureau of Mines report.

III

The Board of Appeals decision holds, in effect, that the results accomplished according to the present invention are no better than those accomplished according to the Bureau of Mines process. As a matter of fact, this is not the case. The applicants were formerly employees of the Bureau of Mines and are familiar with the process described in the Bureau of Mines report. The process according to the Bureau of Mines report involves the two steps of first adding ferrous sulphate to remove iron and arsenic and then following this with a xanthate treatment to remove cobalt and nickel. This was stage 1 of the Bureau of Mines work. The current efficiency was relatively low and the purity of the solution not as high as desired. Stage 2 of the Bureau of Mines work was the substitution of hydrogen sulphide or ammonium sulphide for the xanthate of stage 1. This increased the current efficiency slightly and produced a purer manganese solution. The current efficiency at this stage was about 50 to 55. It was after stage 2 had been reached that applicants entered the picture in their work at the Bureau of Mines. Applicants added on the step of treating the solution with iron following the sulphide treatment. This raised the current efficiency to about 60-70 and considerably improved the deposition of manganese. Stages 1 and 2 of the Bureau of Mines report were carried out by investigators other than the present applicants. It did not occur to these prior investigators to add on the step of adding iron subsequent to a preliminary sulphide treatment. In view of the fact that it did not occur to prior investigators of the Bureau of Mines, and in view of the fact that it produces substantially superior results, it is submitted that invention was involved.

Some of the information embodied herein has only just been received. Otherwise it would have been presented earlier.

Respectfully submitted,

STEBBINS, BLENKO & WEBB,
Attorneys for Applicants.

April 14, 1948.

Decision on Petition for Reconsideration.

Appeal No. 14,259

DH

IN THE UNITED STATES PATENT OFFICE
BEFORE THE BOARD OF APPEALS

Ex parte Frank W. Woodman and Miles B. Royer
Application for Patent filed February 10, 1942, Serial
No. 430,258. Purification of Manganese Salt Solutions.
Messrs. Stebbins, Blenko and Webb for appellants.

ON PETITION FOR RECONSIDERATION

This is a petition for reconsideration of the Board's decision dated March 26, 1948.

Appellants argue, in Section III of the petition, that the current efficiency in their process is about 60-70, whereas the current efficiency in Stage 2 of the Bureau of Mines work was about 50 to 55. These figures are given in the petition as "facts" but the statement is not in the form of an affidavit so that we cannot consider the allegations as to the alleged facts relative to the current efficiency in appellants' process.

Furthermore, the current efficiency is not, *per se*, an element of the claimed invention but is a feature of the deposition process not claimed.

Appellants have made a statement under oath as to the current efficiency under certain conditions. See specification, page 8, Table III. These efficiencies are generally of the order of those obtained by Hannay et al and, while a current efficiency of 63.06 was obtained in Test 4, this was due to the increase in voltage and current density and not to the method of purifying the solutions because Solutions 3 and 4 are identical.

The petition is granted as to reconsideration, but is denied as to any change in our decision.

BOARD OF APPEALS

F. J. PORTER,
Examiner-in-Chief.

L. P. McCANN,
Examiner-in-Chief.

MICHAEL HERTZ
Examiner-in-Chief.
(Acting)

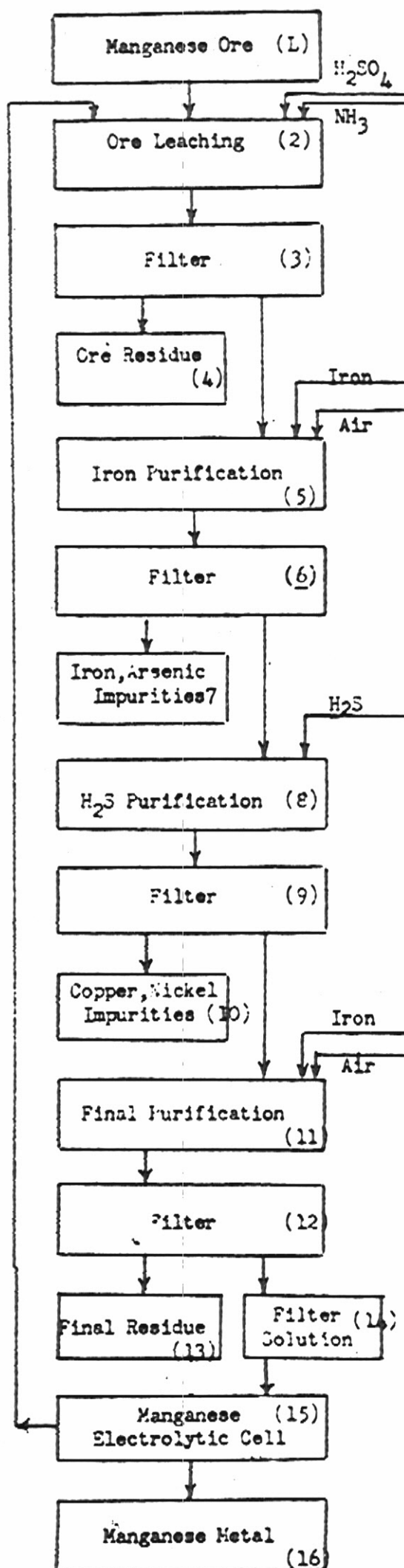
September 28, 1948

Messrs. STEBBINS, BLENKO & WEBB,
1319 Farmers Bank Building,
Pittsburgh 22, Pennsylvania.

Flow Diagram

Remarks

Plaintiff's EXHIBIT NO. 2



(1) Subjected to a reducing roast

(2) The leach solution contains manganese sulphate and ammonium sulphate and impurities such as the sulphates of iron, arsenic, copper, nickel, etc.

(3)

(5) The solution is oxidized with air. This precipitates the iron, which carries down with it the arsenic if sufficient iron is present in the solution. Additional iron is added if an insufficient amount is obtainable from the leaching of the ore. This step does not precipitate the copper or nickel because they are present in the solution as sulphates.

(6) The precipitate of iron and arsenic is filtered off.

(8) The filtrate is treated with hydrogen sulphide to convert the sulphates of copper and nickel to sulphides some of which precipitates and are filtered off. However, copper and nickel sulphides are somewhat soluble in the solution so that the precipitation of copper and nickel sulphides is not complete and small amounts of copper and nickel sulphides remain dissolved in the solution. The solution is filtered and is sparkling clear but contains traces of copper and nickel sulphides in solution. This solution is not suitable for electrodepositing manganese.

(11) Iron (as ferrous sulphate) is added to the solution containing copper and nickel sulphides in solution. Some of the ferrous sulphate reacts with the copper sulphide and with the nickel sulphide to form iron-copper and iron-nickel sulphides, such compounds being less soluble than copper sulphide and nickel sulphide and therefore precipitate.

Any excess iron precipitates as iron hydroxide. The precipitate is then filtered off, the filtrate being suitable for the electrodepositing of manganese.

JAN 10 1951

HARRY M. HULL, Clerk

JULY 1938

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UNITED STATES
DEPARTMENT OF THE INTERIOR
HAROLD L. ICKES, SECRETARY

BUREAU OF MINES
JOHN W. FINCH, DIRECTOR

EXHIBIT 4

REPORT OF INVESTIGATIONS

PROGRESS REPORTS - METALLURGICAL DIVISION

23. ELECTROMETALLURGICAL INVESTIGATIONS

ELECTROLYTIC MANGANESE, BY S. M. SHELTON, M. B. ROYER, AND A. P. TOWNE.

BOULDER CITY, NEV., ELECTROMETALLURGICAL LABORATORY, BY J. KOSTER AND
R. G. KNICKERBOCKER.

PULLMAN, WASH., UNIT, ELECTROMETALLURGICAL SECTION, BY H. A. DOERNER.



No attempt was made to obtain optimum particle size for roasting and leaching. It was found that the crushing and grinding, as given, furnished a satisfactory particle size for the porous ore. Subsequent tests of a hard, dense, manganese ore proved that a much finer grinding would be required for efficient leaching. It is to be expected that the best grinding conditions will depend on the ore texture, and large differences in texture are encountered with different manganese ores.

Roasting

The reduction of manganese dioxide to manganous oxide in ore has been studied and reported by the Bureau of Mines.^{6/} Ore is heated to 500° to 700° C. for 30 to 60 minutes in a strongly reducing atmosphere, and is cooled in a reducing atmosphere to less than 100° C. before contact with air. Hot manganous oxide is unstable and easily oxidizable. It is imperative that the heated ore be protected carefully from oxidation until the temperature is less than 100° C. No evidence of oxidation of the reduced calcine at room temperature has been observed, although the calcine frequently was exposed to the air for a week or more during operation of the experimental pilot plant.

A rotating kiln-type furnace, with cooling chamber attached, was constructed as shown in figure 1. The rotating tube within the firebox was made of Duriron reinforced tube. The cooling-chamber tube was made of ordinary pipe steel. The feed hopper was held against the end of the tube with a spring holder, as shown, to allow for thermal expansion and contraction of the tube and at the same time to make a reasonable tight joint. The feed hopper was kept full of crushed ore and the rate of feed into the tube was controlled by a plunger. Cooled reduced ore at the end of the cooling chamber fell through a cast-iron pipe tee connected to the cooling chamber with a slip joint, and into a receiving hopper made of zinc-coated sheet iron and tightly connected to the tee by a pipe nipple.

Thermocouples inserted in the firebox, as shown, were calibrated against thermocouples inserted through the feed end, inside of the tube, with the tube rotating and before the furnace was charged with ore. The furnace was rotated with a 1-horsepower electric motor and reducing gear through a chain drive at a rate of 6.7 revolutions per minute.

Ore was roasted in batches of 85 pounds to fill the receiving hopper. With continuous discharge of the calcine, the capacity of the furnace would be approximately 1 ton of ore per 24 hours in continuous operation. Roasting procedure was to heat the furnace to the desired temperature with an oil burner. Baffles in the firebox were adjusted to obtain equal temperatures at the two thermocouples. When a tube temperature of 650° C. was attained, ore was hand-fed through the hopper. One hour was required to feed a batch of 85 pounds. Constant temperature in the furnace was

^{6/} Clevenger, G. H., and Caron, M. H., The Treatment of Manganese-Silver Ores: Bull. 226, Bureau of Mines, 1925, 110 pp.

maintained for 2 hours after feeding, and an additional hour of rotating was allowed for the ore to reach the receiving hopper. An excess of "true oil" - type 7/ city gas was fed through the tube to a burner outlet during the entire operation. A typical analysis of the gas, furnished by the gas company, is as follows:

Constituent	Percent	Constituent	Percent
CO	8.8	O ₂	0.3
Illuminants	2.5	N ₂	4.5
CH ₄	29.2	H ₂ S.....	Trace.
H ₂	53.5	B.t.u. per cubic foot.	553
CO ₂	1.2		

No attempt was made to measure gas consumption with batch operation because no relationship could be drawn between consumption for batch operation and consumption for continuous operation.

The ore, initially black, changed to a pale-green color during the roasting process.

Leaching and Purification

Laboratory tests have shown that at least 99 percent of the manganese content of the ore can be leached readily with a two-stage leaching procedure. Limited facilities in the experimental pilot plant made it necessary to restrict the procedure to a single-stage batch leach. The procedure and flow lines used in the experimental pilot plant for leaching the calcine and purifying the leach solution are represented in the flow sheet (fig. 2).

Calcine and spent electrolyte, with enough acid added to produce a neutral leach solution containing 25 grams manganese per liter, were mixed in two 100-liter barrels with wooden impellers. A typical batch consisted of 13 pounds (5.9 kilograms) of calcine, 80 liters of solution containing 200 grams per liter of ammonium sulphate, 9 grams per liter of manganese sulphate, and 44 grams per liter of sulphuric acid. After a 2-hour agitation period, the pulp was drawn off and filtered in a recessed-plate type, cast-iron, pressure filter press. The filtrate contained 200 grams per liter of ammonium sulphate, 25 grams per liter of manganese as manganese sulphate, and small quantities of impurities.

The 80-liter leaching batches were filtered into a lead-lined tank until a purification batch of 400 liters accumulated. Typical analysis of a purification batch before treatment is:

Constituent	Grams per liter	Constituent	Grams per liter
Mn	25.25	Cu.....	<0.0005
NH ₄ SO ₄ ..	196.8	Ni.....	.01
Fe.....	.056	Co.....	.009
As.....	.0002	Pb.....	<.001

7/ Gas made from the destructive distillation of crude oil.

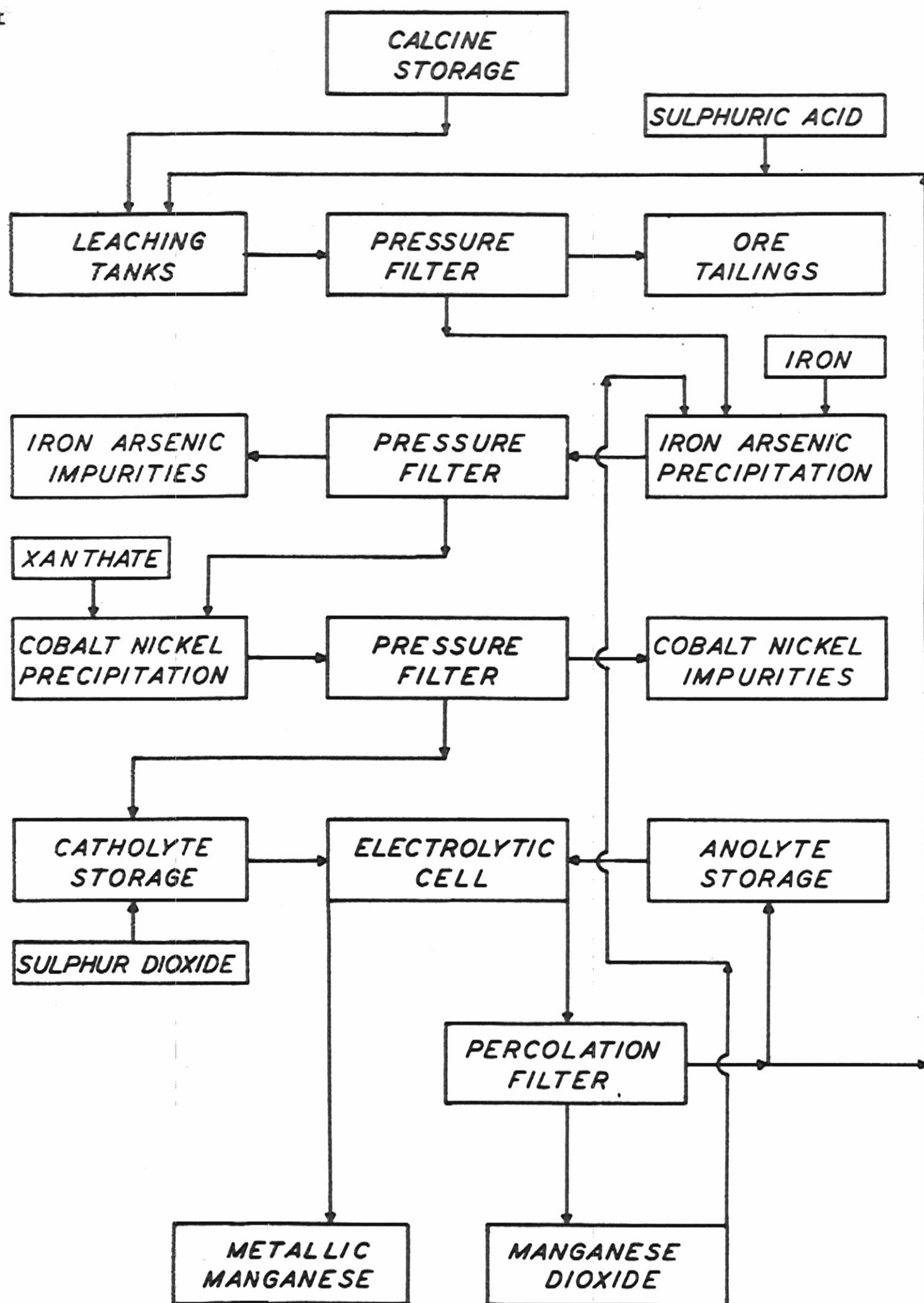


Figure 2.- Flow sheet for leaching ore and purifying leach solution in the experimental pilot plant.

Harmful impurities, including iron, copper, arsenic, cobalt, and nickel, if present in the ore, must be reduced to low concentrations. Methods for purification developed in the electrolytic zinc industry ^{8/} are applicable, with certain modifications, to the purification of manganese sulphate solution. Methods of purification have not been explored completely.

Manganese hydrolyzes and precipitates from a manganese sulphate solution when the solution is more basic than a pH of 7.0, provided that ammonium sulphate is absent from the solution. In the presence of ammonium sulphate, however, manganese can be held in solution at a pH greater than 10.0, whereas acid and ammonical zinc sulphate solutions are quite stable.

The maximum pH obtainable with a zinc oxide leach is on the order of 5.3 to 5.8. Manganous oxide ore leaches readily to a pH of 7.5 to 8.0. The zinc ion has a great affinity for sulphide ion in a neutral solution and interferes with the precipitation of many impurities as sulphides. Manganous sulphide is more soluble and can be used as a precipitating agent for several impurities - the degree of purification depending, of course, on the solubility of the sulphide compound formed.

IMPURITIES IN MANGANESE ELECTROLYTE

Individual impurities in manganese electrolyte will be considered.

Iron. - It has been found that the solubility of ferric iron in manganese sulphate solution in the presence of ammonium sulphate is less than 0.3 mg per liter at a pH range of 7.0 to 8.0. The manganous ion is more readily leachable and apparently replaces the ferrous iron in solution in the leaching stage to a large degree. Oxidation of the remaining ferrous iron with air or, more conveniently, with manganese dioxide anode slime leads to iron precipitation, as shown in the procedure.

Arsenic. - In line with electrolytic zinc practice, arsenic is either chemically combined or adsorbed in the precipitation of ferric iron, leaving concentrations of arsenic at less than 0.05 mg per liter at a solution pH of 7.0, provided that sufficient iron is precipitated. It was found that a ferrous-iron concentration of 0.1 gram per liter was desirable for reducing the arsenic content from 1 mg per liter to less than 0.05 mg per liter. Accordingly, ferrous iron in the form of metallic iron or ferrous sulphate was added to the impure leach solution when the ferrous-iron content was less than 0.1 gm per liter.

^{8/} Laist, F., Frick, F.F., Elton, J.O., and Caples, R.B., Electrolytic Zinc Plant of Anaconda Copper Mining Co. at Great Falls, Mont.: Trans., A.I.M.E., vol. 64, 1920, p. 699.
Tainton, U.C., and Leyson, L.T., Electrolytic Zinc from Complex Ores: Trans., A.I.M.E., vol. 70, 1924, p. 486.
Snow, W.C., Electrolytic Zinc at Risdon, Tasmania: Trans., A.I.M.E., vol. 121, 1936, p. 482.
Stimmel, B.A., Hannay, W.H., and McBean, K.D., Electrolytic Zinc Plant of the Consolidated Mining and Smelting Co. of Canada, Ltd.: Trans., A.I.M.E., vol. 121, 1936, p. 540.

Copper. - Usual practice of copper removal is replacement either by contact with iron in the form of scrap or with zinc in the form of powder. Both methods are applicable to manganese electrolyte purification, provided that the introduced impurity is removed. Iron can be removed as shown and zinc can be removed by sulphide precipitation. Copper can be precipitated directly with the sulphide ion.

In preliminary work with the ore, which was leached directly with sulphurous acid, and in sulphuric acid after a reducing roast, using powdered coal instead of city gas, copper was usually present in the electrolyte to the extent of 50 mg per liter, or more. The copper content was reduced to concentrations of less than 1 mg per liter by slow circulation through trays of iron nails, which were hand-stirred to maintain clean surfaces.

Leach solutions of calcine, treated as described with city gas, contained 0.5 mg per liter, or less, of copper. The highly selective leaching was due either to complete reduction of more readily leachable manganese in the ore or to the presence of small quantities of hydrogen sulphide in the reducing gas, which formed insoluble copper sulphide in the calcine.

Cobalt and nickel. - Like copper, cobalt and nickel can be precipitated by replacement with powdered zinc and subsequent zinc precipitation. The sulphide ion will precipitate both cobalt and nickel to the extent of the solubility of the respective sulphides.

Alpha nitroso beta naphthol is used as a precipitating agent for cobalt in at least two electrolytic zinc plants 9/, with apparently successful results; but its adaptability to cobalt in manganese electrolyte has not been studied thoroughly.

Xanthates, such as potassium pentasol xanthate and sodium ethyl xanthate, were found to be convenient agents for precipitating both nickel and cobalt from neutral manganese electrolyte and were used for that purpose.

A Purification Batch

Referring to a typical purification batch, analysis given above: Iron to the extent of 0.05 gram per liter as ferrous sulphate was dissolved in the batch, then 0.5 gram per liter manganese dioxide from the spent electrolyte was added, and the solution was agitated for 3 hours. The solution was filtered in all-lead, plate-and frame-type pressure filter press. Analysis of the filtrate showed that iron had dropped to 0.25 mg per liter and arsenic to less than 0.05 mg per liter. The solution from the filter flowed into a second lead-lined tank and was treated with a mixture of 0.3 gram per liter of sodium ethyl xanthate and 0.2 gram per liter of potassium pentasol xanthate. The solution was stirred by hand to obtain

9/ Snow, W. C., Work cited (footnote 8).

Stimmel, B.A., Hannay, W.H., and McBean, K.D., Work cited (footnote 8).

complete dissolution of the reagents, and 6 hours was allowed for complete reaction of the xanthate to precipitate cobalt and nickel. The solution was filtered in an all-lead, plate- and frame-type pressure filter press and pumped into a catholyte feed storage tank, lead-lined, and of 800 liters capacity. Nickel and cobalt concentrations of the catholyte feed were less than 1 mg per liter, respectively.

Sulphur dioxide was added direct to the catholyte feed storage tank until the analysis (using the iodine method) showed approximately 0.1 gram of sulphur dioxide per liter. Addition agents, usually glue or other organic colloids, frequently are added to electrolytes in the electrodeposition of metals to improve the surface texture of the deposit and to prevent the growth of porous areas and "trees." "Goulac", a sulphite paper by-product, was added to the catholyte feed to the extent of 6 mg per liter or 0.04 pound per 100 pounds of electrolytic manganese. Whether the addition agent was beneficial is questionable. Undoubtedly, the solution picked up colloidal material from the new cathode frames, from wooden leaching tanks, and in other contacts with wood in the circuit. Some of the extracted organic compounds are possibly beneficial, others are probably detrimental particularly with respect to current efficiency. It is believed that conclusive results from the effect of colloids, added intentionally or otherwise, can be had only from long-time, large-scale operation.

Spent Electrolyte

The spent electrolyte from the cell contained approximately 3 grams per liter manganese as manganese sulphate, 5 grams per liter manganese suspended as hydrated manganese dioxide, the original approximating 200 grams per liter ammonium sulphate and 30 grams per liter sulphuric acid.

The spent electrolyte was filtered in a percolating-type filter, which consisted of a lead-lined tank 9 by 6 feet and 8 inches deep. A wooden frame was placed over the tank to support a sheet of muslin cloth. The spent electrolyte flowed into the cloth, which filtered out the manganese dioxide and clear solution dripped into the tank to drain into a small storage tank. Part of the solution was then pumped to the anolyte feed storage tank for recirculation through the cells, and the rest was pumped to the leaching tanks and used, with additional acid, to treat calcine again.

Corroding-grade lead was used for all lead linings in the circuit. Small leaks in the lining required frequent addition of ammonium sulphate and sulphuric acid to the circuit and interfered with any study of the cumulative effect of impurities.

ELECTROLYSIS

Power for electrolysis was supplied by a three-unit motor-generator set consisting of two 750-ampere, 6-volt, 1,150-r.p.m., double commutator generators mounted on a common bedplate and direct-connected to a 15-horsepower, 3-phase, 440-volt, 60-cycle motor. A field rheostat was used for voltage adjustment.

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February 1943.

REPORT OF INVESTIGATIONS

Plaintiff's EXHIBIT NO. 5

UNITED STATES DEPARTMENT OF THE INTERIOR - BUREAU OF MINES

MANGANESE INVESTIGATIONS

19. STUDIES IN THE ELECTRODEPOSITION OF MANGANESE

By F. W. Woodman^{1/} and J. H. Jacobs^{2/}CONTENTS

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INTRODUCTION

Manganese is a metal of strategic importance. Each net ton of steel requires approximately 12.5 pounds of manganese, and this, with its many other uses, will require about 1,200,000 tons of 50-percent ore in 1942. Until recently the United States imported about 96 percent of its requirements from Russia, South America, and South Africa, but with the war conditions in Europe and the lack of ships for transportation even from those sources where ore is still available the Nation will be dependent to a great extent upon domestic sources for ore.

Although there are large quantities of manganese ore^{3/} in the United States, most of it is low-grade and cannot be used for the production of ferromanganese.

Since the electrolytic production of manganese offers a method whereby the extensive deposits of low-grade manganese of this country can be utilized, work was undertaken at the Boulder City (Nevada) Experiment Station of the Bureau of Mines to test existing procedures and to develop new methods whereby manganese could be produced by electrolysis more economically than heretofore.

Although manganese for use in steel can be produced by electrolysis, it is believed that at the end of the present emergency there will be sufficient demand for pure manganese as an alloying element to support an electrolytic-manganese industry. New uses for electrolytic manganese as a base for nonferrous alloys have been reviewed by Dean and co-workers.^{4/}

It is to be emphasized that the results shown in this paper were obtained on a small scale laboratory basis. At present they are being tested in the 1,000 pound pilot plant at Boulder City, Nevada.

PREVIOUS WORK ON ELECTROWINNING OF MANGANESE

The work of early investigators on the electrolysis of manganese solutions has been reviewed by Shelton.^{5/} Until the method of continuous production of

^{3/} Dean, R. S., and others: Manganese: Its Occurrence, Milling, and Metallurgy: Bureau of Mines Inf. Circs. 6768, 6769, 6770, 6771, and 6772, 1934.

^{4/} Dean, R. S., and others, Manganese and Its Alloys: Bureau of Mines Rept. of Investigations 3477, 1939, 47 pp.

^{5/} Shelton, S. M., Electrolysis of Manganese Solutions. Bureau of Mines, Rept. of Investigations 3322, 1936, 64 pp.

manganese by electrolysis was perfected by Shelton^{6/} and coworkers,^{7/ 8/} no practical procedure had been devised. The method as developed by the Bureau of Mines will be described here only briefly.

The manganese oxide ore was reduced in a rotating kiln-type furnace at 650° C. in an atmosphere of "city" gas. The calcine was leached with spent electrolyte and enough sulfuric acid to produce a neutral leach solution containing 25 grams manganese per liter as manganese sulfate and 200 grams per liter of ammonium sulfate.

Arsenic was removed from the solution by the addition of 0.05 gram iron per liter as ferrous sulfate followed by oxidation with manganese dioxide and aeration, which precipitated the iron as ferric hydroxide. The solution free from iron and arsenic was treated with a mixture of 0.3 gram per liter of sodium ethyl xanthate and 0.2 gram per liter of potassium pentasol xanthate. After standing 6 hours, the nickel and cobalt had been precipitated by the xanthate and were removed by filtration. Sulfur dioxide was added to the solution to the extent of 0.1 gram per liter.

The above purified solution was then electrolyzed in a lead-lined cell with the cathodes suspended in canvas-covered wooden frames, which formed diaphragms between the anodes and cathodes. The cathodes were of 10-gage, 17-percent chromium steel and the anodes were 1/4-inch corroding-grade lead.

During operations the manganese content of the catholyte feed was 24 to 26 grams per liter, pH 7.2 to 7.6; the manganese content of the catholyte within the frame was 8 to 10 grams per liter, pH 9.0 to 9.2; the manganese content of the anolyte was 3 to 6 grams per liter, and the sulfuric acid content of 25 to 30 grams per liter. The current density was maintained between 18 and 20 amperes per square foot. About 20 percent of the manganese fed to the cell was deposited at the anode as a hydrated manganese compound. An average current efficiency of 50 percent was obtained over a 48-hour deposition period. The metallic manganese deposited contained 0.20 to 0.30 percent sulfur, which would make the metal undesirable for many purposes.

6/ Work cited in footnote 5

7/ Shelton, S. M., and others, Progress Reports, Metallurgical Division. 23. Electrometallurgical Investigations: Bureau of Mines Rept. of Investigations 3406, 1938, 28 pp.

8/ Koster, J., and Shelton, S. M., Electrolytic Manganese: Eng. and Min. Jour., vol. 137, 1936, p. 510.

Dean^{9/} and coworkers improved the process with the aim of obtaining metallic manganese substantially free from sulfur. The purification step for the removal of cobalt and nickel was changed. It was found that the cobalt and nickel could be precipitated from solution by the addition of sulfide ion as barium or ammonium sulfides. Electrolytic manganese produced from solutions purified by sulfide contained little or no sulfur.

Preliminary tests also indicated that the leach solutions could be purified by the addition of powdered metallic manganese, which precipitated the impurities. Although this method of purification showed promise, further investigation was not made at that time.

The results of the studies of the former Metallurgical Division of the Bureau of Mines were encouraging enough to justify commercial exploitation of the process, and the Electro Manganese Corporation, Knoxville, Tenn., has been operating a 2-ton plant successfully for 3 years.

PRESENT WORK ON ELECTROWINNING OF MANGANESE

Discussion

This work on the electrodeposition of manganese was undertaken with the definite aim of improving certain procedures of the process formerly advocated and thereby lowering cost of production. Some of the main points of the process upon which investigations were planned are as follows:

1. Roasting
2. Leaching and purification
3. Ammonium sulfate and manganese sulfate concentrations.
4. Current density and manganese strip.
5. Anodes and cathodes.
6. Addition agents.
7. Cell design and diaphragms.

These investigations have been carried out in the laboratory on a small scale, and many improvements have been made. The improvements are now being tested in the pilot plant at Boulder City, and the results will be reported at a later date.

^{9/} Work cited in footnote 4

Ore Used in Electrolytic-Manganese Test Work

All of the experimental work on the electrolytic manganese process performed in the Boulder City laboratories was on ore from the Three Kids mine. This ore body is in Las Vegas Wash, near Lake Mead, in Clark County, Nevada. This ore was chosen because of the large size of the deposit and its availability, as it is only 12 miles from Boulder City.

The ore is an earthy material, or wad, with which is intermixed small amounts of psilomelane and manganite and acicular crystals. The nonmetallic portion of the ore is composed of small amounts of quartz, mica, gypsum, kaolinite or decomposed tuff, opal, and minor amounts of undetermined silicates.

The ore is a light, porous, amorphous-appearing mass that breaks down on wetting to granular particles and slimes. Owing to its extreme porosity, the ore can be reduced and acid-leached without fine grinding.

A typical analysis of the ore received at the Boulder City station is as follows:

	Percent
Manganese	27.7
Iron	1.10
Arsenic	.10
Cobalt	Trace
Nickel	Trace
Copper	0.27
Lead	.017
CaO	4.75
MgO	3.24
P	.05
SiO ₂	20.50

Roasting

As the manganese in the Three Kids ore is quadravalent, it must be reduced to the lower states of oxidation, which are soluble in dilute sulfuric acid. The object of the reduction is to obtain the maximum sulfuric acid-soluble manganese for leaching with spent electrolyte from the electrolytic process.

It can be seen from the above analysis that there is virtually no elimination of any impurities by the roasting.

Leaching and Purification

The problem of leaching the manganese calcine with acid and subsequent removal of impurities is a very important step in the electrolytic manganese process. Obviously, it is desirable to obtain the maximum extraction of the manganese from the calcine and to remove impurities from the leach solution to a minimum concentration. The exact limits of impurities in the purified electrolyte that will allow manganese to be deposited electrolytically are not known and would be difficult to determine because the presence of a combination of impurities has a different effect than when the impurities are present singly. Also, the permissible amounts of impurities vary with the various plating factors, such as type of cathode, current density, and manganese and ammonium sulfate concentration.

The following general procedure for leaching the reduced ore has been found to be satisfactory. The proper amount of calcine to give the desired manganese concentration is added to the lead-lined leach tank containing spent electrolyte, and the solution is agitated. During the first half hour any additional acid necessary is added to the leach to bring the pH of the solution to approximately 2. It was found that at a pH of 2.0 maximum extraction of the manganese was obtained. The leach is agitated for 1-1/2 hours with the pH held at 2.0. At the end of this time more calcine is added to the tank, until a pH of 6.0 is reached. This usually requires 15 to 20 percent of the original weight of calcine and about 1-1/2 hours agitation. Agitation is then stopped, and the residue is allowed to settle. When a thoroughly reduced calcine is being leached, an extraction of 90 percent can be made. This method is, in effect, a two-stage leach, but it is accomplished in the same tank. It was found that a distinct two-stage leach step give very little improvement in manganese extractions. A neutral leach - that is, a leach wherein the pH is not allowed to go below 6.0 at any time - will give only a 75 percent manganese extraction. It is desirable to finish the leach at a pH of 6.0, because this is the pH necessary for the purification steps and precipitates the iron extracted in the acid leach. Commercial ammonium sulfate and sulfuric acid are used throughout. The temperature of the leach is kept as low as possible, as manganese extraction decreases with increasing temperature.

The raw leach solution is decanted from the leach tails into another lead-lined tank for the first purification step. The cobalt, nickel, iron, arsenic, lead, copper, etc., are then removed by the addition of sulfide ion at a pH of 6.0 to 6.5. The amount of sulfide ion necessary to remove the

impurities will vary with the amount in the solution being treated. In treating the leach solution from Three Kids calcine, 0.4 gram of sulfide ion per liter was found to be enough to remove the impurities. The solution is agitated for 1 hour and is then allowed to stand for 8 hours before filtering.

Tests were made with hydrogen sulfide, ammonium sulfide, barium sulfide, and calcium sulfide as the sulfiding agent. All of these removed the various metallic impurities, with the exception of calcium sulfide. However, it is believed that calcium sulfide could be used in combination with one of the other sulfides. It has the advantage that granular calcium sulfate is formed, which aids filtration of the sulfide precipitate. When the sulfide is added to the raw leach solution, pink manganese sulfide is precipitated first, which then redissolves, and the other metallic sulfides are precipitated. It is necessary to precipitate a small amount of manganese sulfide to insure complete removal of the impurities.

After the precipitated sulfides have been removed from the solution by filtration it is necessary to eliminate any residual sulfide from the solution. This can be accomplished by vigorous aeration, which precipitates sulfur, followed by filtration.

It was found that solutions treated in this manner were usually satisfactory for plating. However, this purification method did not provide the degree of certainty necessary for a commercial operation.

After extensive experimentation it was found that if 0.1 gram per liter of iron was added to the sulfide filtrate and precipitated as the hydroxide the solution was cleared of all residual sulfides as well as any colloidal material that remained in the solution. Although it has been impossible to determine by chemical analysis what is removed from the solution by the ferric hydroxide, it has been proved by several months of laboratory operation that this final purification step definitely improves the solution for electrolysis. The iron may be added as ferric or ferrous sulfate.

Small-scale laboratory experiments have indicated that powdered electrolytic manganese can be substituted for the sulfide for the removal of metallic impurities from the leach solution. Powdered manganese has the advantage that no impurity is being introduced into the solution and that purification can be accomplished in a few minutes, in comparison with the 8 hours required for sulfide purification. Laboratory tests showed that the copper, arsenic, cobalt, zinc, lead, and nickel were removed by 2 grams of powdered manganese (-150 mesh) per liter in 5 minutes. The iron remaining in solution is removed then by precipitation as the hydroxide.

As current efficiency depends on so many inter-related factors, it is difficult to determine the individual effect of these factors.

As was pointed out before, unless the ammonium sulfate concentration is sufficient to prevent hydrolysis of the manganese in the catholyte, current efficiency will be low; and unless the manganese concentration is about 20 grams per liter for the higher current densities, current efficiency will be lowered.

Trees and nodules tend to lower current efficiency, but this effect can be minimized by the use of addition agents.

The pH can be decreased with no effect upon current efficiency if the current density is increased at the same time. If the pH is below 2.0, however, resolution of the deposit will begin, and consequently efficiency will drop.

To obtain the maximum current efficiency impurities should be removed from the electrolyte to a minimum concentration.

When plating under the optimum conditions, an average current efficiency of 65 percent will be obtained over a 24-hour period.

Current efficiency drops with increase in time of deposition, and the exact plating time will be an economic compromise between efficiency and labor costs.

Summary

The results of laboratory work on the electrolysis of manganese sulfate solutions have been discussed and may be summarized in the following optimum conditions:

Purified solution	- 40 to 50 g/l manganese as $MnSO_4$.
	- 125 to 150 g/l ammonium sulfate.
	- 0.10 g/l sulfur dioxide.
	- 8 to 16 mg/l glue.
Anolyte	- 10 to 20 g/l manganese as manganese sulfate.
	- 25 to 40 g/l H_2SO_4 .
	- 125 to 150 g/l ammonium sulfate.
Current density	- 40 to 60 amps./sq. ft.
pH of catholyte	- 6.0 to 7.2
Anodes	- Pb-1 percent Ag.
Cathodes	- Aluminum treated with aluminum powder.

First Two Years Operation of the Bureau of Mines Electrolytic Manganese Pilot Plant at Boulder City, Nevada

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(New York Meeting, February 1944)

THE present paper records a chapter in the history of the development of an electrolytic manganese industry in the United States.¹

A relatively large pilot plant at Boulder City, Nev., for the production of electrolytic manganese was conceived as part of the national defense program to make this country independent of foreign importation of manganese ore.

The first authorization, in November 1940, however, was for a plant of only several hundred pounds capacity. Improvements in process and subsequent additions to some sections authorized by subsequent appropriations have enabled the plant to produce as much as 2000 lb. of manganese a day for substantial periods of time.

Since in pilot-plant operation frequent changes are made in the flowsheet, the electrolytic manganese plant was constructed so that equipment could be rearranged with a minimum of expense and time. Several different kinds of the various types of equipment were installed for many

of the operations, so that the one most suitable for the process might be chosen.

Pilot-plant operations were begun in November 1941 and have been continuous except for brief shutdowns for installation of new equipment. More than one-half million pounds of manganese have been produced. The improvements in process, selection of equipment, and operational procedure developed are recorded here.

DEVELOPMENT OF THE PROCESS

The work of early investigators on the electrolysis of manganese solutions has been reviewed by Shelton.² Until the method of continuous production of manganese by electrolysis was perfected by Shelton²⁻⁴ and coworkers, no practical procedure had been devised. The method as originally developed by the Bureau of Mines will be described here only briefly.

The manganese dioxide ore was reduced in a rotating kiln-type furnace at 650°C. in an atmosphere of "city" gas. The calcine was leached with spent electrolyte and enough sulphuric acid to produce a neutral leach solution containing 25 grams manganese per liter as manganese sulphate and 200 grams per liter of ammonium sulphate.

Arsenic was removed from the solution by the addition of 0.05 gram iron per liter as ferrous sulphate followed by oxidation with manganese dioxide, and aeration, which precipitated the iron as ferric hydroxide. The solution, free from iron

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¹ References are at the end of the paper.

and arsenic, was treated with a mixture of 0.3 gram per liter of sodium ethyl xanthate and 0.2 gram per liter of potassium pentasol xanthate. After standing 6 hr., the nickel and cobalt had been precipitated by the xanthate and were removed by filtration. Sulphur dioxide was added to the solution to the extent of 0.1 gram per liter.

The purified solution was then electrolyzed in a lead-lined cell with the cathodes suspended in canvas-covered wooden frames, which formed diaphragms between the anodes and cathodes. The cathodes were of 10-gauge, 17 per cent chromium steel, and the anodes were $\frac{1}{4}$ in. corroding-grade lead.

During operations the manganese content of the catholyte feed was 24 to 25 grams per liter (pH, 7.2 to 7.6); the manganese content of the catholyte within the frame was 8 to 10 grams per liter (pH, 9.0 to 9.5); the manganese content of the anolyte was 3 to 6 grams per liter and the sulphuric acid content 25 to 30 grams per liter. The cathode current density was maintained between 18 and 20 amp. per sq. ft. About 20 per cent of the manganese fed to the cell was deposited at the anode as a hydrated manganese compound. An average current efficiency of 50 per cent was obtained over a 48-hr. deposition period. The metallic manganese deposited contained 0.20 to 0.30 per cent sulphur, which would make the metal undesirable for many purposes.

Dean¹ and coworkers improved the process with the aim of obtaining metallic manganese substantially free from sulphur. The purification step for the removal of cobalt and nickel was changed. It was found that the cobalt and nickel could be precipitated from solution by the addition of sulphide ion as barium or ammonium sulphides. Electrolytic manganese produced from solutions purified by sulphide contained little or no sulphur.

Preliminary tests also indicated that the leach solution could be purified by the

addition of powdered metallic manganese, which precipitated the impurities. Although this method of purification showed promise, it has not been demonstrated on a large scale.

The results of the work of the early Bureau of Mines investigators was sufficiently encouraging to justify construction of a commercial plant at Knoxville, Tenn., by the Electro Manganese Corporation,⁵ which has been operating a 2-ton plant successfully since 1938. The plant capacity was increased to 4 tons per day in early 1943. This plant is using the basic process as developed by the Bureau of Mines in 1936-1938.

Construction of the Boulder City pilot plant was begun in April 1941. While the pilot plant was under construction, extensive laboratory investigations were carried on and the work reported by Woodman and Jacobs;⁶ it will be briefly reviewed here.

Results of small-scale experiments showed that the reduction of manganese ores could be accomplished with coal, coke, natural gas, butane or oil. Although the reduction could be most easily controlled and carried out using oil or a reducing gas, the geographical location of a plant would determine which of the five reducing agents would be most satisfactory from the economic standpoint.

The calcine was leached in small lead-lined wooden tanks to a pH of 2.0 for 1½ hr.; then the solution was neutralized to a pH of 6.0 with calcine. An extraction of 90 per cent of the manganese was obtained. The raw solution was decanted from the leached tails and the solution purified by the addition of 0.4 gram of hydrogen sulphide per liter of solution. All of the metallic impurities were precipitated as sulphides and were removed by filtration on a plate and frame filter press. This filtrate is theoretically pure but does contain colloidal sulphur and colloidal metallic sulphides and organic matter from the

ammonium sulphate. It was found that if 0.1 gram of iron per liter of solution was added as copperas and the solution was oxidized with air and filtered, all of the aforementioned materials were removed. This was an important improvement, because it always ensured a pure solution for electrolysis.

In the early Bureau of Mines process, the cathodes in the electrolytic cell were suspended in diaphragm-covered compartments. A normal operating cell contained 28 anodes and 27 cathodes. This design was necessary because of the manganese oxides formed at the anodes, but this cell had many undesirable features because each cathode compartment had to be fed separately; consequently, manganese was being plated from 27 different catholytes. This involved careful control of pH and solution content. As the quantity of catholyte was so small, it was difficult to prevent the pH from becoming too high, with consequent precipitation of manganese hydroxide. Also, the cells could not be operated at a current density above 30 to 35 amp. per sq. ft., because the pH would become too high, causing the manganese to precipitate.

It was decided that these difficulties could be overcome by placing the anodes inside the diaphragm compartments. However, before this could be done, it was necessary to have an anode at which little or no manganese oxides would be precipitated. A lead-tin-cobalt alloy was reported by Fink⁷ to prevent the formation of manganese oxides, but an anode of this alloy is difficult to make and has a rather short life. A perforated lead-silver anode was developed, which reduced the amount of manganese precipitated at the anode from 25 per cent for pure lead to 1.0 per cent.

The use of lead-silver anodes made possible a design wherein the anodes were inside the diaphragm compartments and all the cathodes were plating from the

same catholyte. This simplified cell control and allowed the electrodeposition to be carried out at cathode-current densities as high as 70 amp. per sq. foot.

The optimum conditions for the electro-winning of manganese were given by Woodman and Jacobs as follows:

Purified feed solution.....	40 to 50 grams per liter Mn as $MnSO_4$ 125 to 150 grams per liter ammonium sulphate 0.10 grams per liter sulphur dioxide 8 to 16 mg. per liter glue
Anolyte.....	10-20 grams per liter Mn as $MnSO_4$ 25 to 40 grams per liter sulphuric acid 125 to 150 grams per liter ammonium sulphate
Current density...	40 to 60 amp. per sq. foot
Catholyte pH.....	6.0 to 7.2
Anodes.....	Pb and 1 per cent Ag inside diaphragm
Cathodes.....	$\frac{3}{16}$ -in. aluminum treated with aluminum powder
Diaphragms.....	canvas or micropore rubber
Voltage.....	4.5 to 5.4
Kw-hr. per lb. Mn.	3.6 to 3.9
Current efficiency..	60 to 65 per cent

THE PILOT PLANT

All of the pilot-plant buildings are of steel construction covered with corrugated, galvanized-iron sheeting. The crushing plant is in a separate small building. Roasting, leaching and purification equipment is installed in the hydrometallurgical building, with all storage tanks and thickeners in the open. The cell room and generator are in a separate building. The flowsheet of the plant is shown in Fig. 1.

Ore is delivered to the crushing plant by trucks into a wooden bin through a grizzly. Oversize ore is broken through the grizzly by hand. Crushing is accomplished by a jaw crusher and rolls in closed circuit with a vibrating screen. An inclined belt con-

veyor delivers the crushed ore to the hydrometallurgical building, where a Jeffrey vibrating conveyor distributes it to any of ten 5-ton steel storage bins. From

of the ore; one is a 5-ft., 10-hearth Skinner furnace with muffled hearths, so that it is indirectly fired, and the other is a Traylor multitube rotary kiln consisting of five

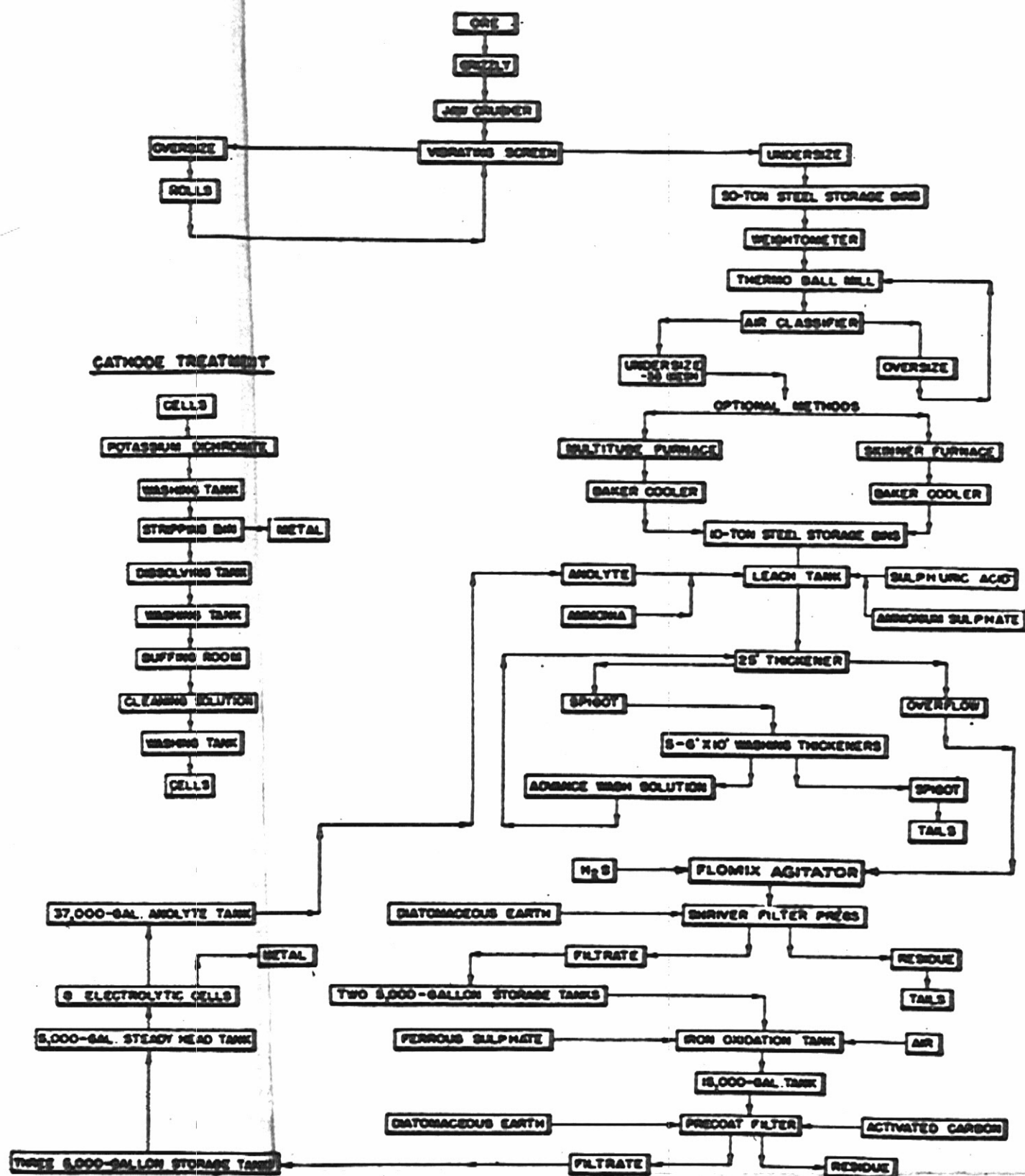


FIG. 1.—FLOWSHEET OF ELECTROLYTIC MANGANESE PILOT PLANT.

the storage bins, the ore is weighed in buggies and fed to a Hardinge thermal ball mill equipped with an air classifier, where it is ground dry to -35-mesh.

Two furnaces are available for reduction

10-in. alloy-steel tubes inside a brick-lined shell. Ore travels through the tubes and the fire is on the outside of the tubes. Each furnace discharges into a Baker cooler, where the calcine is cooled to below 100°C.

before entering the atmosphere. This is necessary to prevent reoxidation of the reduced ore. Both furnaces are fired with oil, and the roasting is carried out at 700° to 750°C. Reduction is accomplished by dropping oil on the ore as it enters the multitube furnace. Calcine discharges from the coolers into ore buggies and is transported to a 10-ton steel bin or directly to the leaching tanks. Since manganous oxide reoxidizes rapidly in air, it is not stored more than 24 hours.

Leaching is done in 3500-gal. batches in two 8 by 10-ft. brick-lined steel tanks equipped with stainless-steel propeller-type agitators. Spent electrolyte from the cells, containing 8 to 10 grams per liter manganese as manganese sulphate, 135 to 140 grams per liter ammonium sulphate and 43 to 50 grams per liter sulphuric acid, is drawn into a leach tank. Reduced ore is then added and leached for 1 hr., or until the pH has risen to 3.0. Sulphuric acid and ammonium sulphate are added as needed, so that the finished leach contains 32 to 36 grams manganese and 135 to 140 grams ammonium sulphate per liter. After the desired pH and manganese concentration have been reached, the leach is neutralized by the addition of ammonia gas. The resultant neutral solution is pumped to a 25-ft., acidproof steel thickener. Spigot discharge from the thickener containing barren tails, ferric hydroxide and aluminum hydroxide is washed countercurrently in five 10-ft. acidproof steel thickeners. After being washed free of manganese and ammonium sulphate, the residue is pumped to a tailing pond. Oliver diaphragm slurry pumps are used on all the thickeners and for discharging the leach tanks.

In addition to manganese and ammonium sulphate, the neutral leach solution, which overflows from the 25-ft. thickeners, contains small amounts of iron, arsenic, copper, zinc, lead, nickel, cobalt and molybdenum. All these impurities must be removed before electrolysis.

As the first step in purification of the solution, it flows by gravity from the neutral thickener overflow storage tank through a Nettco Flomix, where hydrogen sulphide gas is added. The Flomix is a small, stainless-steel, totally enclosed agitator flanged to fit a 3-in. line. The solutions are vigorously agitated by the Flomix, and complete precipitation of the impurities as sulphides results. After the solution leaves the Flomix, it is pumped directly to a Shriver plate-and-frame filter press, where the precipitated sulfides are removed from the solution.

Although the solution is now free of metallic impurities, it contains colloidal sulphur, colloidal metallic sulphides and organic matter that is introduced with the ammonium sulphate. These materials are removed by adding copperas and oxidizing the iron with air. The iron precipitates as ferric hydroxide; this precipitate absorbs the sulphur and colloids and also removes any residual arsenic and molybdenum that were not precipitated by hydrogen sulphide. An Oliver precoat filter is used to filter the iron hydroxide from the solution. A mixture of diatomaceous earth and activated carbon is used as the filter precoat. The resultant solution is now pure and ready for electrolysis. It is stored in four 10 by 10-ft. acidproof steel tanks, to be drawn into the cell room as needed.

In the cell room, electrolysis is carried out in eight lead-lined wooden tanks, 9.5 by 2.5 by 3.5 ft. inside dimensions and connected in series by a 2 by 7-in. copper busbar suspended on the side of the cells. Each tank has a capacity of 28 anodes and 27 cathodes, spaced 3½ in. from anode to anode, and is supported by glass blocks on concrete piers. The cathodes are held in place on their busbar by cadmium-plated copper clips, and the anodes are bolted directly to the bar. Power is furnished by a 450-kw. twin motor-generator set driven by a 700-hp. synchronous motor. Purified solution containing 34 to 36 grams per liter

manganese as manganese sulphate, 135 to 140 grams per liter ammonium sulphate and 0.1 gram per liter sulphur dioxide flows to the cells through a 2-in. lead line on the

the diaphragms in a common anolyte was found to be advantageous to re the position of the anodes and cathode reasons that will be discussed later; t

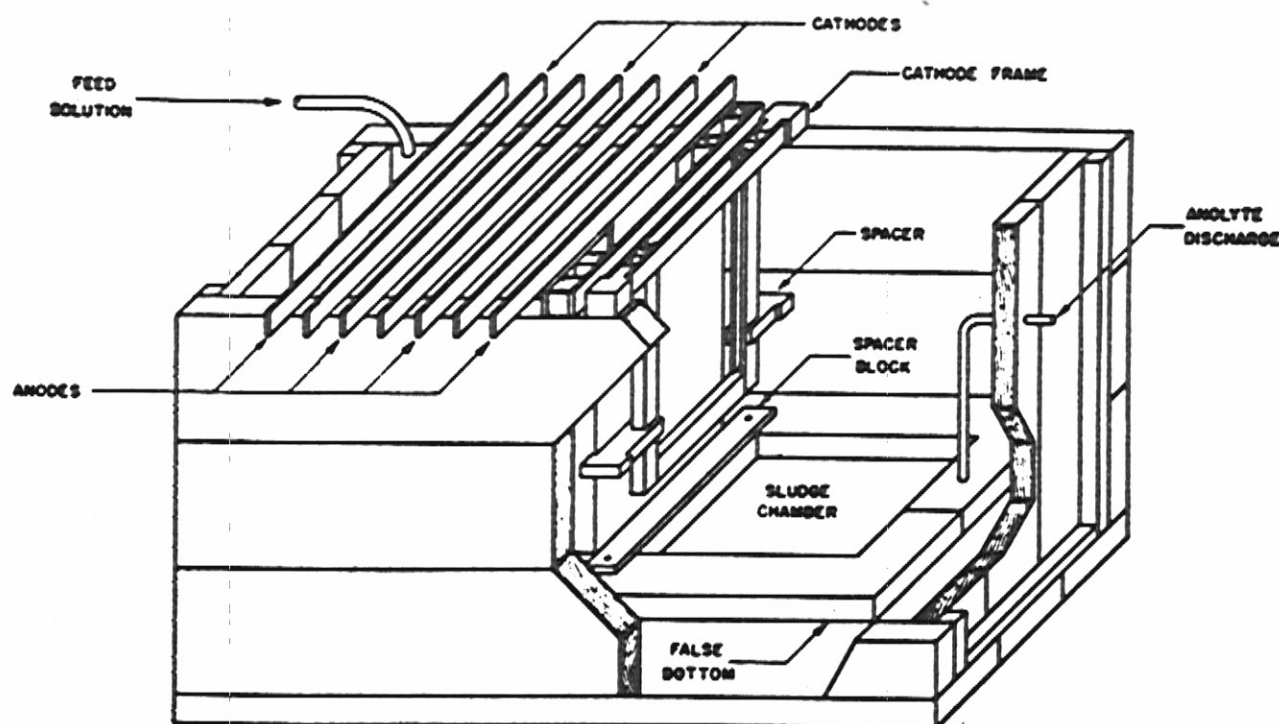


FIG. 2.—CELL USED IN PILOT PLANT FOR MAKING ELECTROLYTIC MANGANESE.

side of the tanks. Flow rate is controlled by rubber-lined diaphragm valves at each cell. Sulphur dioxide is added to the solution in the main line as it enters the cell room, to prevent precipitation of manganese hydroxide.

The cathodes are type 316 stainless steel, 18 by 36 by 16-in. gauge. Two copper strips $3\frac{1}{2}$ by $1\frac{1}{2}$ in., covered with lead, are brazed along the top of the cathode to carry the current. A semimirror finish is maintained on the cathode by buffing every fourth day. The anodes, 15 by 32 by $\frac{1}{4}$ in., composed of 99 per cent lead, 1 per cent silver, are cast and drilled with $1\frac{3}{8}$ -in. holes so that 40 per cent of the area is void. This is necessary to increase the anode-current density, which minimizes the formation of manganese oxides.

As manganese cannot be electrodeposited efficiently from acid solution, the anolyte and catholyte must be separated by a diaphragm. In the original process, each cathode was in a separate canvas-covered frame, which necessitated a separate feed line to each. The anodes were outside of

fore the cell now used in the pilot plant the anodes placed inside canvas-covered wooden frames, which are open at bottom. The cell has a false bottom 1 above the main bottom, in which a tangular area the width of the anode fr is cut out. This false bottom is comp by the anode frames and wooden s blocks, which fit between the anode fra ensuring proper spacing. In this mann lower compartment is formed in the into which the oxide at the anode Phenolic resin frames hold the cathod place in the cell (Fig. 2).

Solution flows through the cells a lows: The purified solution entering catholyte from the feed line along th of the cell flows through the canvas phragm into the anolyte compart down into the lower compartment fo by the false bottom, and is then disch from the cell through a 2-in. lead rising from the false bottom at one e the cell and out through the side a desired height. A lead-lined wood la conveys the spent electrolyte to a ta

sement, where it is pumped to the
ing plant for leaching more reduced

electrolyte in the cells is cooled by
uting cold water through lead coils
cells. The water is cooled in the sum-
y an ammonia compressor and by an
rative cooler in the winter.

ls must be broken down at the end
8 weeks for cleaning and replacement
aphragms. Calcium sulphate crystals
on the anolyte side of the canvas
ragm, reducing the porosity to the
where the solution will not flow
igh it.

electrodeposition conditions are as fol-

e.....	99 per cent Pb, 1 Ag 15 by 32 by 1/4 in. 40 per cent void 28 anodes per cell
ode.....	Type 316 stainless steel 18 by 36 by 16-in. gauge 27 cathodes per cell
ent density.	Anode: 81 to 90 amp. per sq. ft. Cathode: 45 to 50 amp. per sq. ft.
voltage....	5.0-5.3
l solution...	Mn: 34 to 36 grams per liter (NH ₄) ₂ SO ₄ : 135 to 140 grams per liter SO ₂ : 0.15 gram per liter
holyte.....	Mn: 8 to 10 grams per liter (NH ₄) ₂ SO ₄ : 155 grams per liter (calculated from am- monia content) SO ₂ : 0.10 gram per liter
lyte.....	Mn: 8 to 10 grams per liter (NH ₄) ₂ SO ₄ : 135 to 140 grams per liter H ₂ SO ₄ : 43 to 50 grams per liter
aphragm.....	18-oz. canvas
ation of electrolysis....	24 hr.
nds Mn per cathode....	10 to 12
ent efficiency.....	60 to 65 per cent
ter deposition for 24 hr., the cathodes removed from the cells and dipped in a cent solution of potassium or sodium	

dichromate, to prevent oxidation of the
manganese. They are then washed in a
spray tank and air-dried. The deposited
manganese is stripped from the cathode by
flexing and striking with a rubber mallet,
with a recovery of 98.5 to 99.5 per cent of
the metal. The small quantity remaining
on the cathode is dissolved in a tank con-
taining spent electrolyte from the cells.
After the residual manganese is removed,
the plates are washed in a spray tank.
Every fourth day the cathodes are buffed
and then cleaned with a standard alkaline
soap cleaner. After being washed free of
cleaner, they are ready for the cells.

Pilot-plant operations have been con-
tinuous, with few exceptions, and the effect
of the variables of the process has been
studied. As many of the factors in the
process can be varied over wide ranges, it
was frequently necessary deliberately to
operate the plant under conditions that
were not conducive to efficient operation,
to obtain the required data.

A research laboratory was maintained in
conjunction with the pilot plant at all
times, and the work of both was closely
coordinated. The results reported here were
obtained in small laboratory equipment
and in the large plant equipment. Where
the results of the two were relatively con-
cordant, no distinction will be made, but
where large variations were encountered it
will be so noted.

Although the pilot plant was operated
primarily for the purpose of obtaining data,
more than 550,000 lb. of metallic manga-
nese was produced during the first 2 years
of operation.

ORE

The ore used in the pilot-plant work is
from the Three Kids mine, Las Vegas
Wash, near Lake Mead, Clark County,
Nev. It was chosen because of its availa-
bility and the fact that it is similar to ore
from many other deposits in the country.
The manganese is present as the dioxide,

the reduction are drawn off at the discharge end of the furnace. An attempt was made to operate the multitube with countercurrent flow of the reducing gas but because of the arrangement of the five tubes it could not be done successfully.

TABLE 5.—*Reduction Roasting in Multitube Rotary Kiln*

Wet feed, lb.	96.174
Mn in feed, per cent.	32.53
Dry feed, lb.	92.876
Water in feed, per cent.	3.43
Calcine, lb.	82.341
Mn in calcine, per cent.	37.90
Reducing oil (No. 200), gal. per ton dry feed.	14.75
Heating oil (No. 200), gal. per ton dry feed.	36.21
Temperature in hot zone.	750°C.
Temperature of combustion gas at stack exit.	275°C.
Temperature of reducing gas at stack exit.	175°C.

LEACHING

After the manganese ore has been reduced, it is leached with spent electrolyte, containing sulphuric acid, from the cell room. Spent electrolyte is drawn into the brick-lined leach tank and calcine is added over a 30-min. period. The final volume of the leach is 3400 to 3600 gal. Vigorous agitation is furnished by a stainless-steel ship-type agitator. After the calcine has been charged, sulphuric acid is added to keep the pH at 2.5, which is the finishing point of the leach. Ammonium sulphate also is added at this point as needed to maintain a concentration of 135 to 140 grams per liter in the finished leach solution. A temperature rise of 12° to 16°C. occurs during leaching, and the total time required for leaching is 1¼ to 1½ hr. A manganese extraction of 98 to 99 per cent is obtained. There is considerable sliming of the ore during leaching, as shown in Table 2. Table 6 shows the solution concentrations before and after the leaching. Since the leach residue must be washed thoroughly to remove manganese sulphate and ammonium sulphate, it is necessary to allow for dilution by the wash waters in arriving at the final manganese and ammonium sulphate concentrations.

After the leach is finished at a pH of 2.5, it must be neutralized to a pH of 6.5. This can be done by ammonia or by adding cal-

TABLE 6.—*Solution Concentrations during Leaching*
GRAMS PER LITER

Constituent	Spent Electrolyte	Leach Solution at pH 2.5	Leach Solution at pH 6.5	Leach Solution, after Residue is Washed
Mn.	10.5	37.5	36.5	34.7
(NH ₄) ₂ SO ₄	136.2	137.8	144.6	137.6
Fe.	0.0015	0.16	0.001	0.001
As.	0.0005	0.02	0.0018	0.0017
Ni.	<.001	<0.001	<0.001	<0.001
Co.	<.001	<0.001	<0.001	<0.001
Cu.	0.006	0.04	0.01	0.0095
SiO ₂	0.02	1.29	0.02	0.0285
MgO.	11.8	12.4	12.4	11.8
CaO.	1.20	1.25	1.25	1.20
Al ₂ O ₃	0.01	0.29	0.01	0.01
Mo.	0.0007	0.008	0.005	0.0048

cine. If calcine is used as the neutralizing agent, the over-all leach extraction is lowered from 98 to 99 per cent to 92 to 95 per cent. If ammonia is used, the higher leach extraction is obtained and the amount of ammonium sulphate needed is reduced. It is a matter of economics as to which is used, and in the pilot plant it is cheaper to use ammonia. When the leach is neutralized iron and aluminum hydroxides, molybdenum, arsenic and silicates precipitate. The leach is pumped to a thickener from which the overflow is sent to purification. Five countercurrent thickeners wash the spigot product from the leach thickener, and the washed tails are discarded. Water averaging 5 per cent of the leach volume

TABLE 7.—*Settling of Neutral Leach**

Time, Min.	Settlement, In.	Solution above Solids
15	0	No break
30	6¾	Floccular
40	7¾	Slightly floccular
50	8½	Slightly floccular
60	9	Slightly floccular
75	9¾	Slightly floccular
105	9¾	Very slightly floccular

* pH, 6.4; temperature, 42°C.; percentage solids 2.8; sp. gr. sol., 1.17; sp. gr. solids, 2.8.

is added at the head of the washing thickeners. Advance wash solution, containing 75 to 90 grams per liter ammonium sulphate and 16 to 20 grams per liter manganese, flows to the leach thickeners.

The leach contains 2.5 to 3 per cent solids and has a rather slow settling rate, as shown in Table 7.

The sulphuric acid consumption averages 0.25 lb. per pound of manganese leached, owing to the insoluble sulphates, such as calcium, etc., formed in the leach.

An extensive investigation was carried out on the method of removing the leached residue from the solution and washing it free from manganese sulphate and ammonium sulphate. Filtration is not satisfactory, since the large amount of slimes and hydroxides in the residue cause the filter rate to be so slow that it is not economical. A Bird centrifuge was used for several tests, but once again a separation could not be made at an economical rate. Washing in countercurrent thickeners is the most satisfactory method, since they do not require much attention and a washed residue containing less than 1.5 per cent manganese can be obtained.

PURIFICATION

After the manganese has been leached from the ore and the residue removed from the solution, impurities such as As, Co, Ni, Cu, Fe, etc., must be removed before the solution is ready for electrolysis. The purification procedure depends on impurities in the solution. However, it has been found that solution from all the ores tested could be purified by the addition of sulphide ions. Hydrogen sulphide is used in the pilot plant, since it is added easily and is the most economical form of sulphide ion; but barium, sodium, or ammonium sulphides are satisfactory from the standpoint of purification.

The clear overflow from the leach-solution thickeners, which has a pH of 6.4 to 6.6, is stored until ready for use. It flows

from the storage tank to a stainless-steel Nettco Flomix, and hydrogen sulphide is added in the solution line. The Flomix is a totally enclosed double agitator, flanged in the lead-solution line. As the solution flows through the Flomix it is violently agitated, which completes precipitation of the metallic sulphides. As the solution leaves the Flomix, it flows into a surge tank, where it ages 15 to 30 min. and is pumped to a Shriver plate-and-frame filter press. The filter press is precoated with diatomaceous earth, to improve the filter rate.

It was found that the impurities were completely removed if the solution was filtered after 15 to 30 min. aging time. If the precipitated sulphides are allowed to remain in contact with the solution for several hours, re-solution takes place. When the hydrogen sulphide is added to the solution, orange manganese sulphide precipitates; this redissolves and the impurities are precipitated. However, 0.7 to 1.0 gram per liter of manganese is lost as the sulphide during the purification. The hydrogen sulphide necessary to precipitate the metallic impurities completely is 0.10 to 0.15 gram per liter of solution. If any slimes are present in the solution as it comes from the leach thickener, the consumption of hydrogen sulphide is greatly increased, therefore it is necessary to operate the thickener so that there is a minimum of slimes in the overflow. An analysis of the solution before and after sulphide purification is shown in Table 8.

After the metallic impurities have been removed by precipitation as sulphides, the solution contains colloidal sulphur, colloidal sulphides and a small amount of residual arsenic and molybdenum. It was found that the addition of 0.10 gram per liter iron as copperas, followed by oxidation and precipitation of ferric hydroxide, led to adsorption of the colloids, arsenic and molybdenum. The solution leaving the filter press after removal of the metallic sulphides flows to a brick-lined tank, simi-

lar to the leach tanks, and a solution of copperas is added. The solution is mixed by an Agitair agitator with a hollow shaft. Air is added through the hollow shaft, and the iron is completely oxidized and precipitated. The iron is precipitated in 3500-gal. batches. After all the iron is oxidized and precipitated (which is determined by testing with potassium thiocyanate), the solution is pumped to a storage tank, where it is allowed to age 4 to 6 hr. It is then

TABLE 8.—*Purification of Solution*
GRAMS PER LITER

Constituent	Solution before Purification	Solution after H ₂ S Purification	Solution after Fe Purification
Mn.....	35.8	35.1	34.4
(NH ₄) ₂ SO ₄	139.6	139.5	139.2
Cu.....	0.04	0.00008	0.00008
Fe.....	0.003	0.0015	0.0002
As.....	0.0014	0.0006	0.00015
Ni.....	<0.001	<0.001	<0.001
Co.....	<0.001	<0.001	<0.001
Mo.....	0.0005	0.0005	0.0003

filtered on an Oliver precoat drum filter. A mixture of diatomaceous earth and activated carbon removes organic material, which enters the solution with the ammonium sulphate. After filtration, the solution is sent to storage to be drawn into the cell room as needed. Table 8 shows the analysis of the solution before and after removal of iron.

The iron oxidation is carried out at room temperature at a pH of 6.5 to 7.0 and requires 40 to 60 min. to complete the reaction, which can be speeded by heating. As manganese is oxidized, even at a pH of 6.5 to 7.0, there is a precipitation of 0.5 to 1.0 gram per liter of manganese hydroxide. This is not lost, however, as the cuttings from the precoat filter are returned to the leach tank.

ELECTROLYSIS

The successful electrowinning of manganese from relatively pure solutions of manganese sulphate and ammonium sul-

phate depends upon a combination of many factors, such as concentration of solution, current density, pH of solution, cathode and anode material, temperature, and rate of flow to cell. It is almost impossible to consider any of these variables separately, since nearly all of them depend on the others, and the limits of one variable cannot be specified without defining the other conditions very closely. It is in this respect that the electrowinning of manganese demands more delicate control than that of other metals, such as zinc and copper.

DESIGN OF CELL AND FRAME

The early design of the cell is described on page 2. With the development of the lead-silver anode, it became possible to reverse the position of the anodes and cathodes, owing to the small amount of oxide produced at the anode. The principal advantages gained from this arrangement are: (1) Each cell can be controlled by one feed line instead of the 27 formerly used; (2) all of the cathodes are suspended in a common catholyte, which leads to uniformity of deposition; (3) the catholyte volume is tripled, thereby making control of pH and solution concentrations easier and less critical; (4) as the catholyte volume is so large, the cells may be operated at a higher current density and a larger strip of manganese can be made. This greatly decreases the necessary size of the leaching and purification plant.

The cell design as now used was described previously and shown in Fig. 2. This design was the ultimate result of several different types that were used in the pilot plant. The first cells in the pilot plant were merely a reversal of the anodes and cathodes in the original cell, with tubes leading from the anolyte compartment through the side of the cell for discharge of anolyte. Although this was an improvement, the discharge tubes became plugged, and despite the fact that there was only a small amount of oxide formed, it caused the

A paper presented at the Eighty-Sixth General Meeting, held at Buffalo, N. Y., October 14, 1914, E. A. Lowenheim presiding.

JAN 10 1951

HARRY E. HULL, Clerk

Plaintiff's EXHIBIT NO. 7

THE EFFECT OF CERTAIN VARIABLES ON THE ELECTRODEPOSITION OF MANGANESE¹

By J. H. JACOBS,² P. E. CHURCHWARD³ AND R. G. KNICKERBOCKER⁴

ABSTRACT

An electrolytic manganese pilot plant having a present daily capacity of 2,400 lb. (1,090 kg.) has been operated by the U. S. Bureau of Mines for the past 2½ years. This paper records the results obtained on the effect of certain variables on the electrodeposition of manganese, namely, time of deposition, cathode current density and cell temperature. It was found that the current density and time of deposition could be varied over a wide range, with only a slight variation in current efficiency. The power requirement, however, does vary considerably. A cell temperature of 35°C was found to be the optimum for operation. A decrease in temperature below 35°C has only a slight effect on current efficiency and greatly increases the voltage. An increase above 35°C results in a nodular and arboreal deposit with rapid lowering of current efficiency. The optimum conditions for the operation of electrolytic manganese cells were found to be 45 to 50 amp./sq. ft. (4.9 to 5.4 amp./dm.²) cathode current density; 35°C cell temperature; and 32-hour deposition time.

INTRODUCTION

A relatively large pilot plant at Boulder City, Nevada, for the production of electrolytic manganese was conceived as part of the U. S. Department of the Interior National Defense Program to make this country independent of foreign imports of manganese. The first authorization (in November, 1940) was for a plant of only several hundred pounds capacity, but improvements and additions increased the capacity to 2,400 lb. (1,090 kg.) per day. The plant has been operating continuously since November, 1941, with the exception of brief shut-downs for installation of new equipment. More than a 1,000,000 lb. (454,000 kg.) of manganese metal have been produced. This paper is concerned with the effect of certain electrodeposition variables in the process: current density, time of deposition, and cell temperatures.

¹ Presented by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Manuscript received July 1, 1944.

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THE ELECTROLYTIC MANGANESE PROCESS

Only a very brief description of the process as a whole will be given here, since it has been completely reported in the literature. A bibliography is appended which covers development of the process during the last few years.

In the pilot plant at Boulder City, manganese ore is crushed through 48 mesh (0.33 mm. hole) and reduced in a 10-hearth, 5 ft. (1.5 m.) diameter Skinner muffle furnace. The roast is necessary to reduce the higher oxides of manganese present in the ore to manganous oxide, which is soluble in sulfuric acid.

The reduced ore is leached with spent electrolyte from the cells, and the residue is separated from the solution in a 25 ft. (7.6 m.) thickener and washed in five 10 ft. (3 m.) countercurrent thickeners. The raw leach solution is maintained at a pH of 6.5 and contains 33 to 35 g./L Mn, 130 to 135 g./L ammonium sulfate, and small quantities of impurities, such as copper, arsenic, molybdenum, nickel, cobalt, etc. These impurities are removed as sulfides by precipitation with hydrogen sulfide. (After the precipitated sulfides are removed by filtration, 0.1 g./L Fe as copperas is added to the solution and oxidized and precipitated. The ferric hydroxide precipitate removes any residual arsenic, as well as colloid sulfur and sulfides. After filtration the solution is ready for electrolysis.

Electrolysis is carried out in 8 lead-lined wood cells connected in series by copper busbar. Each cell contains 27 stainless steel (type 316) cathodes (18 x 36 in., or 46 x 91 cm.), each having a submersed area of 6.9 sq. ft. (64 dm.²), and 28 lead +1% silver anodes which are perforated so that they are 40% void. The anode plates are spaced 3.5 in. (9 cm.) in the cell. The cathode area is 1.8 times the anode area; consequently, the anode current density is 1.8 times the cathode current density. This higher density on the anode lowers the amount of manganese oxide, MnO_2 , formed.

The cell contains a false bottom, 10 in. (25 cm.) from the main bottom, from which a rectangular area is cut the width of the anode frames and a length equivalent to the thickness of 28 anode frames and spacer blocks. The anode frames, which are covered with canvas diaphragms and open at the bottom, fit into the rectangular opening, and the false bottom is completed by insertion of wood spacer blocks between the anode frames. In this manner, the cell is divided into an upper compartment and a small lower compartment. The function of the lower compartment is to serve as a reservoir for the manganese oxide which drops off the anodes during electrolysis. The cathodes are suspended in the common aqueous catholyte.

The flow of electrolyte is as follows: The purified feed solution, containing 33 to 35 g./L Mn, 130 to 135 g./L ammonium sulfate and 0.10 g./L SO_4 , is added to the catholyte. From the catholyte compartment the solution flows through the canvas diaphragm into the anolyte compartment, down into the lower compartment and out of the cell through a riser pipe at the end of the cell.

The cells are cooled by water circulating through lead coils in each

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The Electrochemical Society

A paper to be presented at the Ninetieth General Meeting to be held at Toronto, Canada, October 16, 17, 18, 19, 1946.

Preprint 90-35**ADVANCE COPY**

Written discussion of this paper is invited, preferably typewritten and in triplicate, sent to the Secretary, The Electrochemical Society, Inc., Columbia University, New York 27, N. Y. Unless special arrangement is made, discussion of this paper will close November 1, 1946, and any subsequent discussion should preferably be offered in the form of a new paper.

THE EFFECT OF CELL VARIABLES ON THE ELECTROWINNING OF MANGANESE†

By J. H. JACOBS§

ABSTRACT

An electrolytic manganese pilot plant having a daily capacity of 2,000 lb. (900 kg.) has been operated by the Bureau of Mines for the past 5 years. The results recorded are on the effect of certain variables on the electrodeposition of manganese, namely, electrode spacing, rate of feed to the cells, manganese concentration in the cell catholyte, and length of cell operation before cleaning. It was found that in the catholyte outflow the manganese concentration should be maintained at an average of 12 g./L. A decrease or increase of manganese content results in lowered efficiency through scaling and cracking of the deposits. The optimum manganese concentration in the feed was found to be 32 g./L, representing 20 g./L Mn removed from the solution. A greater removal of manganese and, consequently, a lower manganese feed rate increases the catholyte pH, which in turn decreases the current efficiency. When all factors, such as oxide formation at the anode, calcium sulfate precipitation on the diaphragms, and precipitation of manganese hydroxide in the catholyte, are taken into consideration, the cells should be cleaned every seven weeks to obtain most efficient cell operation. There is an increase of about 0.2 volt/cell between the first and seventh week of operation.

INTRODUCTION

Research and development work on a process for the electrowinning of manganese from low-grade ores has been carried on by the Bureau of Mines for the past 10 years. A process for electrowinning of manganese was developed in the Bureau laboratories at Reno, Nev., from 1935 to 1938 by John Koster and S. M. Shelton, working under the guidance of R. S. Dean, now Assistant Director of the Bureau of Mines. In 1940 money was appropriated by Congress for constructing a relatively large manganese pilot plant at Boulder City to operate

† Presented by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Manuscript received July 10, 1946.

§ Senior Metallurgist, Bureau of Mines, Boulder City, Nevada.

the process, using commercial types and sizes of equipment, and to make improvements in the process whereby manganese could be produced at a minimum cost. This plant has been operated continuously since 1941, first under the general supervision of R. G. Knickerbocker, now Chief, Metallurgical Branch of the Bureau of Mines and recently under C. W. Davis, Chief, Boulder City Division. Fig. 1 shows the cell room, which has a daily capacity of over 2,000 lb. (900 kg.) of manganese metal.

More than 1,500,000 lb. (680,000 kg.) of manganese metal has been produced and all phases of the process have been studied and many improvements, particularly in cell design and operation, have been made. This is the second paper discussing the effect of certain cell variables on electrodeposition, and it is concerned with electrode spacing in the cells, rate of feed to the cells, manganese concentration in the cell catholyte, and length of cell operation before cleaning.

ELECTROLYTIC MANGANESE PROCESS

Only a very brief description of the electrolytic manganese process as developed by the Bureau of Mines will be given here. A bibliography is appended which covers development of the process in recent years.

In the pilot plant at Boulder City, manganese ore is crushed to $\frac{3}{4}$ in. (19 mm.) by a jaw crusher and rolls and then ground through 35 mesh (0.4 mm.) in a Hardinge Thermomill. The ore is then reduced in a 10-hearth, 5 ft. (1.5 m.) Skinner muffle furnace at 750° C. The roast is necessary to reduce the higher oxides of manganese to manganous oxide, which is soluble in sulfuric acid. The reduced ore is leached by agitating in tanks with spent electrolyte from the cells which contains 4% to 5% sulfuric acid, and the residue is separated from the solution in a 25 ft. (7.6 m.) thickener and washed in five 10 ft. (3 m.) thickeners. The raw leach solution is maintained at a pH of 6.5 and contains 32 to 34 g./L Mn, 130 to 135 g./L ammonium sulfate, and small amounts of impurities, such as copper, zinc, arsenic, molybdenum, nickel, cobalt, etc. These impurities are precipitated as sulfides with hydrogen sulfide. After the sulfides are removed by filtration, 0.1 g./L Fe as copperas is added to the solution and oxidized and precipitated. The ferric hydroxide precipitate removes any residual arsenic and molybdenum, as well as colloidal sulfur and sulfides. After filtration the solution is ready for electrolysis.

Electrolysis is carried out in 8 lead-lined wooden cells connected electrically in series by copper busbar. Each cell contains 27 type 316 stainless steel* cathodes, 18 x 36 in. x 16 gauge (46 x 81 cm. x 1.6 mm.), and 28 lead + 1% silver anodes, which are made of strips so that the area is equal to 60% of the cathodes. The anodes are spaced 3.5 in. (9 cm.) apart in the cell. The normal time of deposition is 24 hours at a cathode current density of 45 amp./sq. ft. (4.9 amp./dm.²) with resulting current efficiency of 64% to 66%. The cell voltage is 5.2 to 5.3 volts.

The anodes are suspended inside canvas-covered wood frames open at the bottom. The cell contains a false bottom with a rectangular

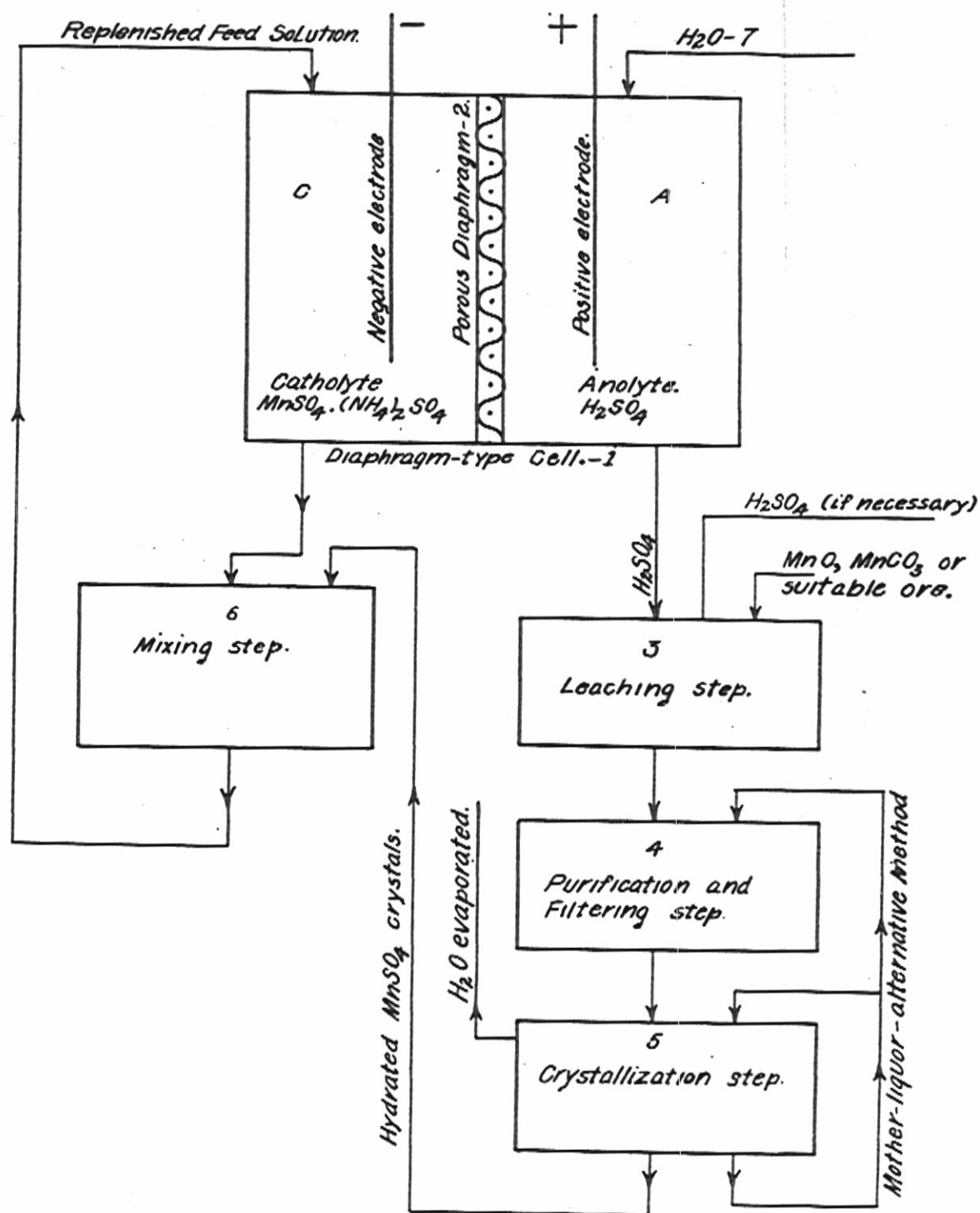
* Ni, 11%; Cr, 18%; Mo, 2%.

Oct. 14, 1941.

W. H. HANNAY ET AL.
ELECTROLYTIC MANGANESE PROCESS

2,259,418

Filed April 3, 1939



WILLIAM HENRY HANNAY
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UNITED STATES PATENT OFFICE

2,259,418

ELECTROLYTIC MANGANESE PROCESS

William Henry Hannay and Basil Joseph Wash,
Trail, British Columbia, Canada, assignors to
The Consolidated Mining & Smelting Company
of Canada, Limited, Montreal, Quebec, Canada,
a corporation of Canada

Application April 3, 1939, Serial No. 265,632

6 Claims. (Cl. 204-105)

Our invention relates to a continuous cyclic process for the extraction of manganese from its ores and the recovery, through electro-deposition, or substantially pure metallic manganese.

We are aware that processes for the extraction of manganese from its ores and the subsequent electro-deposition of metallic manganese from manganous sulphate electrolytes have been the subject of exhaustive investigation for a number of years. Until recent years, however, it has not been feasible to apply electro-chemical methods on a commercial scale, due to the lack of fundamental knowledge of essential operating conditions, the difficulty in maintaining the electrolyte substantially free from impurities which tend to inhibit the deposition of manganese, and the low current efficiency which increases the cost of the manganese above economic limits.

We are also aware that manganese has been electrolytically deposited from electrolytes formed of a solution of manganous sulphate-ammonium sulphate as exemplified by Allmand and Campbell, (Transactions of the Faraday Society, 1924); by technical literature, such as the article by Fink and Kolodney, "Electrodeposition of Metallic Manganese Using Insoluble Anodes" which appeared in Transactions of the Electrochemical Society, 1937; and by Shelton in his U. S. Patent No. 2,119,560.

One of the principal features of our invention resides in the manner in which we continuously electrolyze a separately cycling electrolyte formed of a solution of manganous sulphate and ammonium sulphate, in the cathode compartment of an electrolytic cell, while maintaining, in the anode compartment, an entirely different electrolyte consisting of an aqueous sulphuric acid solution. The two compartments are separated from each other by means of a porous diaphragm; the anolyte and the catholyte do not intermix except to the extent to which there is a transfer of ions through the diaphragm during electrolysis, and to the extent to which sulphuric acid enters the catholyte from the anolyte as the result of diffusion. The additions to the anolyte and catholyte, necessary to maintain the electrolysis, are made separately and each electrolyte is separately discharged from its respective compartment.

A further feature of our invention resides in the manner in which we continuously produce sulphuric acid in the anolyte and, maintaining it at a predetermined concentration by the addi-

tion of water, use the solution thus generated for the subsequent leaching step of the process.

Further features of our invention reside in the manner in which we continuously purify the solution from the leaching step and obtain therefrom hydrated manganous sulphate crystals in a highly purified condition and also in the manner in which we use these purified crystals to replenish the spent catholyte. By the addition of the hydrated manganous sulphate crystals to the depleted catholyte, we form a solution which is suitable for returning to the cathode compartment as feed solution. The concentrations of the constituents of the replenished solution are controlled within predetermined ranges which have been found essential to maintain optimum operating conditions.

The manner in which we operate our process to realize the above and other features will be apparent from the following description and accompanying drawing in which the various steps of the process are illustrated diagrammatically.

Like reference characters refer to like parts throughout the specification and drawing.

The numeral 1 indicates a diaphragm type cell in which the cathode compartment C is separated from the anode compartment A by means of the porous diaphragm 2, formed of such material as alundum. The cathode may be formed of iron, aluminum or of a suitable chromium iron alloy or stainless steel. The anode is preferably formed of lead. While the cell shown has only two compartments, one compartment containing the anolyte and the other, the catholyte, other types of cell, such as a cell divided into three compartments with an anode compartment on each side of the cathode compartment, would be suitable.

The electrolyte circulating through the cathode compartment consists of a compound manganous sulphate-ammonium sulphate solution. The electrolyte in the anode compartment consists of a sulphuric acid solution. Each of the electrolytes is constantly maintained within a predetermined range of concentration.

Water is continuously added to the anolyte at 7. The rate at which the water is added is regulated so that sulphuric acid of a desired concentration is formed on reaction of the water with the sulphate ions entering the anolyte from the cathode compartment.

The numeral 3 indicates the leaching step of the process wherein manganous oxide or manganous carbonate is leached with the sulphuric acid solution withdrawn from the anode com-

partment. Additional sulphuric acid from other sources may be added, if necessary, during this step to replace losses of sulphuric acid which may occur in this or in the subsequent filtering step of the process.

The solution obtained from the leaching step is filtered at 4 and the filtrate is purified to remove impurities such as nickel, cobalt, zinc, lead, iron, arsenic and antimony. While we do not wish to limit the scope of our present invention to any particular purification step, we have found that the use of hydrogen sulphide for the precipitation of metallic impurities present in solutions containing manganese is particularly suitable in this step of the process, after removal of iron by standard methods.

The purified pregnant solution is passed into crystallizer 5 wherein hydrated manganous sulphate is crystallized by heating. We have found that the crystallization step may be readily effected by taking advantage of the fact that, within certain limits, the solubility of manganous sulphate in aqueous solution decreases with an increase in temperature. During this step, some water is removed by evaporation.

The mother-liquor from the crystallizing step may be added to the fresh solution from the purification step and thus re-circulated through the crystallizer or, if the impurities in the mother-liquor should build up to an undesirable extent, they may be removed by returning the solution to the circuit ahead of the purification step.

The crystallized hydrated manganous sulphate is mixed at 6 with spent catholyte withdrawn from the cell. The rate of addition of hydrated manganous sulphate crystals to the spent catholyte is sufficient to replenish the solution adequately before being returned as fresh pregnant feed solution to the cathode compartment. The rate of addition of manganese, in the form of hydrated manganous sulphate, to the spent catholyte is equivalent to the rate at which manganese is deposited on the cathode.

Referring now to specific operating conditions, we have found that the concentrations of ammonium sulphate and manganous sulphate that may be used in the electrolyte may be varied through a relatively wide range. We have found that these two salts may be used in the electrolyte in such relative amounts that the ratio of the weight of ammonia present in the solution to the weight of the manganese present is as low as 0.2. As the use of this minimum ratio is not commercially practicable, we prefer to use concentrations of ammonium sulphate and manganous sulphate such that the weight of ammonia present is not less than 1.4 times the weight of the manganese present. Using our preferred ammonia-manganese ratios, the actual concentrations of ammonium sulphate and of manganous sulphate may be varied within wide limits, which are governed by the maximum solubility of each of these two salts when in the same solution, at temperatures of about 25° C. to 35° C., and by the lowering of the cathode current efficiency to the point at which operation of the cell becomes uneconomical on a commercial scale. When operating the cell with an ammonia-manganese ratio such that the weight of ammonia is at least 1.4 times the weight of the manganese, we prefer to use, in the feed solution, concentrations of the order of 50 grams of ammonia, as NH_3 , per litre and of 35 grams of manganese, as Mn, per litre, the corresponding concentrations of ammonium sulphate and man-

ganous sulphate being approximately 194 and 96 grams per litre respectively.

The catholyte, as it flows through its compartment of the cell, is depleted of manganese by the electro-deposition of that metal. The rate of flow of the solution through the cathode compartment of the cell, and also its composition at entrance and exit are readily regulated to give the most satisfactory results. As electrolysis proceeds, however, the pH of the catholyte, unless suitable provision is made, will drop from the preferred value of about pH 8 to a point where no further deposition of manganese can be obtained.

The drop in pH value of the catholyte is caused by an accumulation of sulphuric acid as a result of the diffusion of sulphuric acid from the anolyte and it is necessary, therefore, to control the pH value of the catholyte by the addition of ammonia.

We have found that when the pH of the solution drops below a value of about 4, the manganese deposits are unsatisfactory, and therefore we prefer to maintain the pH value of the solution within the range of from pH 4 to pH 8 by the addition of ammonia.

We have also found that very satisfactory results are obtained when the rate of flow of the catholyte from the cell is so regulated that the fresh pregnant solution contains about 50 grams of ammonia, as NH_3 , per litre, and 35-40 grams of manganese, as Mn, per litre, and the depleted solution contains about 55 grams of ammonia, as NH_3 , per litre, and 20-25 grams of manganese, as Mn, per litre.

An increase in ammonia content of the outlet solution over the inlet solution is caused by the addition of ammonia to control the pH value of the catholyte, as outlined above, and it will be apparent that the ratio of the weight of ammonia to the weight of manganese is much higher in the depleted solution than it is in the fresh pregnant solution. In the present illustration, for example, the ratio is approximately 1.4 in the feed solution and from 2.0 to 3.0 in the depleted solution.

As set out above, ammonia is added to the catholyte to maintain the pH value thereof within the range of from pH 4 to pH 8 which, in forming ammonium sulphate, adds to the ammonium sulphate already present. If necessary, the spent catholyte may be treated to render the excess ammonia content available for recirculation.

In the anode compartment, the concentration of sulphuric acid in the anolyte is maintained sufficiently high so that the solution obtained from the leaching step, on entering the crystallization step, is nearly saturated with manganous sulphate at ordinary temperatures, and contains from 150 to 200 grams of manganese per litre.

The sulphuric acid solution in the anode compartment is continuously formed by the reaction of the sulphate ions which migrate into that compartment with the water which is added thereto. The total amount of sulphuric acid produced in a given time, of course, depends on the amount of manganese deposited on the cathode in the same time; theoretically, for each pound of manganese deposited, 1.78 pounds of sulphuric acid are produced. We prefer to introduce water into the anode compartment at a rate such that the withdrawn solution contains from 10% to 35% sulphuric acid by weight. Having regard to evaporation losses, losses arising

from the formation of hydrogen and oxygen at the electrodes, and also to the amount of acid that is neutralized in the cathode compartment, the amount of water introduced into the anode compartment is readily adjusted to give a desired concentration of sulphuric acid in the effluent solution.

The temperature of the leaching step is preferably maintained within the range of from 25° C. to 35° C. and an excess of manganous oxide or manganous carbonate is always present in that step to ensure that all the sulphuric acid present is neutralized.

Both manganous oxide and manganous carbonate, when prepared artificially, react readily with sulphuric acid of practically any strength, at temperatures as low as 25° C. On the other hand, manganous carbonate, if available in the form of an ore, requires to be leached with hot acid, and we have found it preferable to leach such an ore at a temperature of about 70° C., to ensure that the manganous carbonate will react readily with sulphuric acid. Leaching at this temperature will produce a supersaturated solution, and it will therefore be necessary, after cooling this solution, to agitate the solution for a sufficient period to dissolve any manganous sulphate which may have crystallized out. When the manganese ore is composed of a higher oxide which is not soluble, the ore is first reduced by conventional methods, such as by a reducing roast, to a lower oxide which is soluble in sulphuric acid.

The purification step of the process is operated within the temperature range of from 25° C. to 35° C., within which range the manganous sulphate is most soluble.

The conditions under which the crystallization step is operated depend upon the rate at which hydrated manganous sulphate crystals must be added to the depleted catholyte solution to maintain the rate of feed of fresh pregnant solution to the cathode compartment. We have found by introducing the purified solution into the crystallizer at about 27° C., the solution contains the greatest concentration of dissolved manganous sulphate. The crystallizer is preferably maintained within the temperature range of from 80° C. to 102° C.

The mother-liquor from the crystallizing step may be recirculated through that step, or, alternatively, it may be passed to the purification step to permit the removal of impurities.

The manganous sulphate crystals leaving the hot crystallizer are presumably combined with one molecule of water of crystallization as expressed by the formula $\text{MnSO}_4 \cdot \text{H}_2\text{O}$. If the crystals are permitted to cool while exposed to the atmosphere, they absorb moisture until their formula may be expressed as $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$. While sufficient water must be added to the catholyte to replace that lost by evaporation and by electrolysis, the addition of water in excess of that amount should be avoided, otherwise the catholyte will be diluted to an undesirable extent. We have found, therefore, that the hydrated manganous sulphate crystals on leaving the crystallizer should be introduced immediately into the mixing step.

The hydrated manganous sulphate crystals are passed to the mixing step of the process into which also flows the depleted catholyte solution withdrawn from the cathode compartment. The mixing can be effected either as a batch process or continuously as desired. The rate of addition

of hydrated manganous sulphate crystals to the spent catholyte is controlled in such a manner that the effluent solution from the mixing step is of the composition desired for the fresh pregnant catholyte entering the cathode compartment, as set out hereinabove.

The cell is preferably operated at a current density of from 2-35 amperes per square foot of cathode surface and the temperature of the electrolyte is maintained at about 25 to 35° C. Under these conditions, we obtain a current efficiency of about 50%, substantially the remainder of the current being consumed in the generation of hydrogen at the cathode and oxygen at the anode.

We have found by operating our process in the manner set out above that the continuous operation thereof is effected on a commercial scale to result in a compact, coherent deposit of substantially pure manganese and at the same time permitting economies in the process which heretofore have been considered impossible to realize.

For example, by maintaining a separately circulating manganous sulphate-ammonium sulphate electrolyte in the cathode compartment and in the anode compartment an electrolyte consisting of an aqueous sulphuric acid solution, we increase the conductivity of the anolyte, thus making possible increased power efficiency. Furthermore, we avoid the formation of manganese dioxide at the anode which, in addition to increasing the circulating load on the system, necessitated shutting down the former type of cell at frequent intervals to remove the precipitated manganese dioxide.

We have found that economic advantages result from the smaller volume of ammonium sulphate and manganous sulphate solution required. Also, the crystallization step effects additional purification of the electrolyte.

It will be apparent, of course, that the process disclosed hereinabove is not limited to the examples set out. Various modifications of the preferred method may be made to meet specific operating conditions without departing from the scope of the appended claims.

What we claim as new and desire to protect by Letters Patent of the United States is:

1. In a continuous process for the electro-deposition of manganese in a diaphragm type cell, the steps of feeding a manganous sulphate-ammonium sulphate electrolyte having a pH value within the range of from pH 4 to pH 8 into the cathode compartment, the anode compartment containing an electrolyte consisting of an aqueous sulphuric acid solution, continuously withdrawing depleted manganous sulphate-ammonium sulphate electrolyte from the cathode compartment and replenishing the manganese content thereof by the addition of manganous sulphate and continuously returning the replenished electrolyte to the cathode compartment, continuously feeding water into the anode compartment in amount sufficient to combine with the sulphate ions migrating through the diaphragm to form an aqueous sulphuric acid solution, and continuously withdrawing aqueous sulphuric acid solution from the anode compartment.

2. In a continuous process for the electro-deposition of manganese in a diaphragm type cell, the steps of feeding a manganous sulphate-ammonium sulphate electrolyte having a pH value within the range of from pH 4 to pH 8 into the cathode compartment, the anode compart-

ment containing an electrolyte consisting of an aqueous sulphuric acid solution, continuously withdrawing depleted manganous sulphate-ammonium sulphate electrolyte from the cathode compartment and replenishing the manganese content thereof by the addition of manganous sulphate and continuously returning the replenished electrolyte to the cathode compartment, maintaining the pH value of the catholyte within the predetermined range by the addition of ammonia, continuously feeding water into the anode compartment in amount sufficient to combine with the sulphate ions migrating through the diaphragm to form an aqueous sulphuric acid solution, and continuously withdrawing aqueous sulphuric acid solution from the anode compartment.

3. In a continuous process for the electro-deposition of manganese in a diaphragm type cell, the steps of feeding a manganous sulphate-ammonium sulphate electrolyte, in which the ratio of the weight of ammonia to manganese is maintained above 0.2 and having a pH value within the range of from pH 4 to pH 8, into the cathode compartment, the anode compartment containing an electrolyte consisting of an aqueous sulphuric acid solution, continuously withdrawing depleted manganous sulphate-ammonium sulphate electrolyte from the cathode compartment and replenishing the manganese content thereof by the addition of manganous sulphate and continuously returning the replenished electrolyte to the cathode compartment, continuously feeding water into the anode compartment in amount sufficient to combine with the sulphate ions migrating through the diaphragm to form an aqueous sulphuric acid solution, and continuously withdrawing aqueous sulphuric acid solution from the anode compartment.

4. In a continuous process for the electro-deposition of manganese in a diaphragm type cell, the steps of feeding a manganous sulphate-ammonium sulphate electrolyte having a pH value within the range of from pH 4 to pH 8 into the cathode compartment, the anode compartment containing an electrolyte consisting of an aqueous sulphuric acid solution, continuously withdrawing depleted manganous sulphate-ammonium sulphate electrolyte from the cathode compartment and replenishing the manganese content thereof by the addition of manganous sulphate and continuously returning the replenished electrolyte to the cathode compartment, continuously feeding water into the anode compartment to combine with the sulphate ions migrating through the diaphragm and in amount sufficient to form an

aqueous sulphuric acid solution containing from 10% to 35% sulphuric acid by weight, and continuously withdrawing aqueous sulphuric acid solution from the anode compartment.

5. A continuous process for the electro-deposition of manganese which comprises electrolyzing a manganous sulphate-ammonium sulphate electrolyte, in which the ratio of the weight of ammonia to manganese is maintained above 1.4 and having a pH value maintained within the range of from pH 4 to pH 8 by the addition of ammonia, in the cathode compartment of a diaphragm type electrolytic cell, the anode compartment containing an electrolyte consisting of aqueous sulphuric acid solution, continuously withdrawing depleted manganous sulphate-ammonium sulphate electrolyte from the cathode compartment and replenishing the manganese content thereof by the addition of manganous sulphate and continuously returning the replenished electrolyte to the cathode compartment, continuously feeding water into the anode compartment in amount sufficient to combine with the sulphate ions migrating through the diaphragm to form an aqueous sulphuric acid solution, and continuously withdrawing aqueous sulphuric acid solution from the anode compartment.

6. A continuous process for the electro-deposition of manganese which comprises electrolyzing a manganous sulphate-ammonium sulphate electrolyte, in which the ratio of the weight of ammonia to manganese is maintained above 1.4 and having a pH value maintained within the range of from pH 4 to pH 8 by the addition of ammonia, in the cathode compartment of a diaphragm type electrolytic cell, the anode compartment containing an electrolyte consisting of an aqueous sulphuric acid solution, continuously withdrawing depleted manganous sulphate-ammonium sulphate electrolyte from the cathode compartment and replenishing the manganese content thereof by the addition of manganous sulphate and continuously returning the replenished electrolyte to the cathode compartment, continuously feeding water into the anode compartment to combine with the sulphate ions migrating through the diaphragm and in amount sufficient to form an aqueous sulphuric acid solution containing from 10% to 35% sulphuric acid by weight and continuously withdrawing aqueous sulphuric acid solution from the anode compartment.

WILLIAM HENRY HANNAY.
BASIL JOSEPH WALSH.

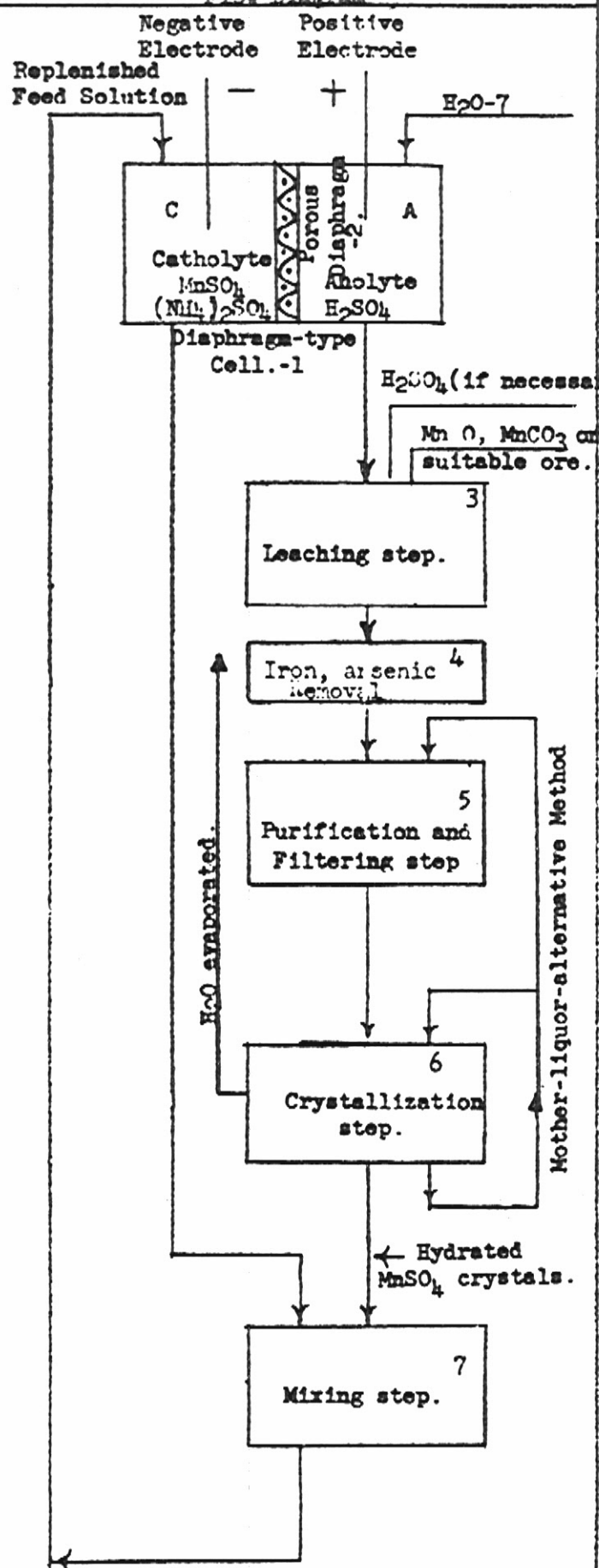
U. S. PATENT

JAN 10 1951

HARRY E. HULL, Clerk

Flow Diagram

Remarks



(2) Plaintiff's Exhibit 10

(3)

(4) Iron is removed by "standard methods" (oxidation by air or manganese dioxide)

(5) The solution is treated with hydrogen sulfide for the precipitation of metallic impurities.

(6) The crystallization step effects additional purification of the electrolyte. (Page 3, line 39).

The mother liquor may be passed to the purification step to permit the removal of impurities. (Page 3, line 50)

(7)

of Sn , and it is seldom advisable to use more than one part of HCl to ten of the solution⁹ (this refers to the reagent HCl , §324).

5. The precipitation takes place better from the warm solutions than from the cold (§81); hence it is directed to warm the solution before passing in the H_2S , and before filtering heat again nearly to boiling. If arsenic be present, the solution should be kept at nearly the boiling point, and the gas passed into the solution for several minutes (§69, 6c).

6. The precipitated sulphides of the metals of the tin and copper group (second group) present a variety of colors, which aid materially in the further analysis of the group. CdS , SnS , As_2S_3 , and As_2S_5 are lemon-yellow; Sb_2S_3 and Sb_2S_5 are orange; SnS , HgS , PbS , Bi_2S_3 , Cu_2S and CuS are black to brownish-black. If too much HCl be present, lead salts frequently precipitate a red double salt of lead chloride and lead sulphide (§57, 6c). Mercuric chloride at first forms a white precipitate of $\text{HgCl}_2 \cdot 2\text{HgS}$, changing from yellow to red, and finally to black with more H_2S , due to the gradual conversion to HgS (§58, 6c).

7. Addition of water to the solution before passing in H_2S may cause the precipitation of the oxychlorides of Sb , Sn or Bi (3d; §70, §71 and §76). These should not be redissolved by the addition of more HCl , as they are readily transposed to the corresponding sulphides by H_2S , and the excess of acid necessary to their resolution may prevent the precipitation of cadmium or cause the formation of the red precipitate with lead chloride.

8. Arsenic when present as arsenic acid is precipitated exceedingly slowly from its cold solutions, and tardily even from the hot solutions. Frequently the other metals of the group may be completely precipitated and removed by filtration, when a further treatment with H_2S causes a precipitation of the arsenic as As_2S_3 from the hot solution. This slow formation of a yellow precipitate is often a very sure indication of the presence of pentad arsenic (§69, 6c, 1).

9. The presence of a strong oxidizing agent as HNO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, FeCl_3 , etc., causes with H_2S the formation of a white precipitate of sulphur (§125, 6c), which is often mistaken as indicating the presence of a second group metal. If the original solution be dark colored, it is advisable to warm with hydrochloric acid and alcohol (§125, 6f and 10) to effect reduction of a possible higher oxidized form of Cr or Mn before the precipitation with H_2S , thus avoiding the unnecessary precipitation of sulphur.

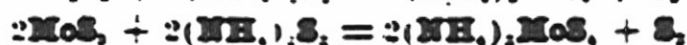
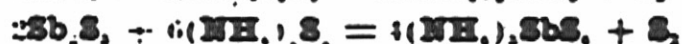
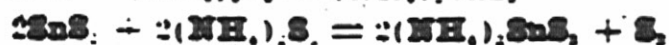
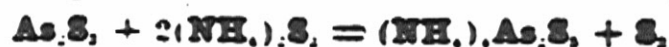
10. Complete precipitation of the metals of the second group with H_2S may fail: (1) from incomplete saturation with the gas (§81, 2); (2) from the presence of too much HCl (§81, 4); (3) from the presence of much pentad arsenic (§69, 6c). The first cause of error may be avoided by careful observance of the directions in note (2). To prevent the second cause of error a portion of the filtrate, after the removal of the precipitate by filtration, should be largely diluted with water (10 volumes) and H_2S (gas or saturated water solution) again added. In case a further precipitate is obtained, the whole of the filtrate should be diluted and again precipitated with H_2S . This should be repeated until the absence of second group metals is assured. If a slow formation of a yellow precipitate indicating As^V is observed, H_2S should be passed into the

⁹ Addition of a strong acid, containing H^+ ions in large quantity, diminishes the already slight dissociation of the H_2S (§64), thus decreasing in number the S^{2-} ions, whose concentration multiplied by that of the metal ions must equal the solubility-product of the sulphide in question, before precipitation can take place. Precipitation of some of the sulphides of the Tin and Copper Group may be entirely prevented in this way.

It frequently happens that addition of water alone will cause precipitation of these sulphides from a strongly acid solution which has been saturated with H_2S . This appears strange in view of the fact that the acid which prevented precipitation and the acid which finally produced it were both diluted by the added water in the same proportion. But as a matter of fact dilution does not have the same effect on a strong acid as on a weak one. Dissociation is always increased by dilution, but in much greater ratio in the case of a weakly-dissociated body as H_2S than where the dissociation of the substance is already practically complete, as in the case of the strong acid. Dilution in the case mentioned increases the relative concentration of the S^{2-} ions and so the solubility-product is reached and precipitation results.

hot solution for fully 30 minutes (Note 5) or the solution should be treated with SO_2 or some other agent for the reduction of As^{V} to As^{III} (§69. 10).

§82. Manipulation.—After the precipitate has been well washed with hot water the point of the filter is pierced with a small stirring rod and the precipitate washed into a test-tube, using as small an amount of water as possible. Yellow ammonium sulphide $(\text{NH}_4)_2\text{S}_2$ (§83. 2) is then added and the precipitate digested for several minutes with warming:



The precipitate is then filtered and washed once or twice with a small amount of $(\text{NH}_4)_2\text{S}_2$, and then with hot water. The filtrate consisting of solutions of the sulphides of **As**, **Sb**, **Sn**, **Au**, **Pt**, **Mo** (*Gr*, *Ir*, *Sc*, *Tc*, *W*, *V*), constitutes the **Tin Group** (Division A of the second group). The precipitate remaining upon the filter, consisting of the sulphides of **Hg**, **Pb**, **Bi**, **Cu**, **Cd** (*Os*, *Pol*, *Rh*, and *Ru*), constitutes the **Copper Group** (Division B of the second group, §95).

§83. Notes.—1. The precipitate of the sulphides of the tin and copper group must be thoroughly washed with hot water (preferably containing H_2S and about one per cent of reagent HCl to prevent the formation of soluble colloidal sulphides (§69. 5c), to insure the removal of the metals of the iron and zinc groups, which would be precipitated on the addition of the ammonium sulphide (§144).

2. Yellow ammonium sulphide, $(\text{NH}_4)_2\text{S}_2$, forms upon allowing the normal sulphide, $(\text{NH}_4)_2\text{S}$, to stand for sometime, or it may be prepared for immediate use by adding sulphur to the freshly prepared normal sulphide (§257. 1). For arsenic sulphides the normal ammonium sulphide may be employed, but the sulphides of antimony are soluble with difficulty, and stannous sulphide is scarcely at all soluble in that reagent; while they are all readily soluble in the yellow polysulphide (*Gr*; §69. §70 and §71).

3. Cupric sulphide, CuS , is sparingly soluble in the yellow ammonium sulphide and will give a grayish-black precipitate upon acidulation with HCl . The sulphides of the tin group are soluble in the fixed alkali sulphides, K_2S and Na_2S ; cupric sulphide is insoluble in these sulphides. Mercuric sulphide, however, is much more soluble in fixed alkali sulphides than cupric sulphide is in the $(\text{NH}_4)_2\text{S}_2$. If copper be present and mercury be absent, it is recommended to use K_2S or Na_2S instead of $(\text{NH}_4)_2\text{S}_2$ for the separation of the second group of sulphides into divisions A (tin group) and B (copper group). If it is Hg^{II} be present, the $(\text{NH}_4)_2\text{S}_2$ should be used, and the presence or absence of traces of copper be determined from a portion of the filtrate from the silver group before the addition of H_2S (§103).

4. The sulphides dissolve more readily in the $(\text{NH}_4)_2\text{S}_2$ when the solution is warmed. An excess of the reagent is to be avoided, as the acidulation of the solution causes the precipitation of sulphur (§256. 3), which may obscure the precipitates of the sulphides present.

COMPARISON OF

Hannay et al Patent No. 2,259,418
 Bureau of Mines Bulletin R. I. 3406
 Woodman et al Serial No. 430,258

Hannay et al - Patent 2,259,418	Bureau - R. I. 3406	Woodman et al Serial No. 430,258
<u>Step 1</u> Removes iron and arsenic present as sulphates by standard methods. (Oxidation with manganese dioxide or air)	<u>Step 1</u> Removes iron and arsenic present as sulphates by oxidation with manganese dioxide. Adds some iron (as ferrous sulphate) before oxidation because the original solution did not contain enough iron to carry down all of the arsenic.	<u>Step 1</u> Removes iron and arsenic present as sulphates by oxidation with air and/or manganese dioxide. Iron (as ferrous sulphate) is added if the original iron present in the solution is insufficient to carry down all the arsenic.
<u>Step 2</u> Precipitates metal impurities with hydrogen sulphide. (Such as nickel, cobalt).	<u>Step 2</u> Precipitates cobalt and nickel as the sulphides with Xanthates.	<u>Step 2</u> Precipitates metal impurities with hydrogen sulphide. (Such as nickel, cobalt)
<u>Step 3</u> Crystallizes manganous sulphate crystals from solution at temperatures of 80°C. to 102°C. Crystallization step effects additional purification of the electrolyte.	<u>Step 3</u> No additional purification used.	<u>Step 3</u> Iron added (usually as ferrous sulphate) to the solution from the sulphide treatment. Further purification results by removing soluble metal sulphides and sulphide ions from the solution. X
<u>Step 4</u> Purified manganous sulphate crystals are dissolved in catholyte from the electrolytic cell and resultant solution is fed to the electrolytic cells.	<u>Step 4</u> SO₂ is added to the Xanthate treated solutions and is fed to the electrolytic cells.	<u>Step 4</u> Purified solutions fed directly to the electrolytic cells.

BRIEF FOR APPELLANT

IN THE
United States Court of Appeals
FOR THE DISTRICT OF COLUMBIA

APPEAL NO. 10928

VANADIUM CORPORATION OF AMERICA,
Appellant,

v.

JOHN A. MARZALL, COMMISSIONER OF PATENTS,
Appellee.

Appeal from a Judgment of the United States District
Court for the District of Columbia.

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Of Counsel:

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STATEMENT OF QUESTIONS PRESENTED.

1. The ultimate question presented to this Court for decision is whether appellant is entitled to the grant of a patent on its process of purifying manganese salt solutions. This involves a determination of

2. Were the individual steps of appellant's process old in the art prior to applicants' invention?

3. Is the sequence of steps used in applicants' process critical and necessary to obtain the desired results?

4. Would it be obvious to one skilled in the art to combine the teachings of the references (Hannay et al. patent No. 2,259,418) and Bureau of Mines Bulletin R. I. 3406) into the particular sequence of steps claimed by applicants, where that particular sequence gives new and improved results and where workers highly skilled in the art and familiar with the teachings of the individual references had been trying unsuccessfully for years to solve the problem?

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IN THE
United States Court of Appeals
FOR THE DISTRICT OF COLUMBIA

APPEAL NO. 10928

VANADIUM CORPORATION OF AMERICA,
Appellant,

v.

JOHN A. MARZALL, COMMISSIONER OF PATENTS,
Appellee.

Appeal from a Judgment of the United States District
Court for the District of Columbia.

BRIEF FOR APPELLANT

I.

JURISDICTIONAL STATEMENT.

On February 10, 1942, Frank W. Woodman and Miles B. Royer filed in the United States Patent Office an application Serial No. 430,258 for "Purification of Manganese Salt Solutions" (App. 74). Upon refusal of the Patent Office Examiner to grant a patent, applicants appealed to the Patent Office Board of Appeals. The Patent Office Board of Appeals in a decision dated March 26, 1948 (App. 98) affirmed the Examiner in his rejection of the appealed claims numbered 22, 26

27 and 28. Applicants on April 15, 1948 filed a petition for reconsideration of the Board of Appeals' decision (App. 102) and the Patent Office Board of Appeals in its decision dated September 28, 1948 adhered to its original decision (App. 107).

On September 25, 1948, Vanadium Corporation of America, assignee of the Woodman and Royer application, filed its Complaint (App. 2) in the District Court of the United States for the District of Columbia under Section 4915 of the Revised Statutes, Civil Action No. 3977-48, praying for an order finding that plaintiff is entitled to receive a patent for the Woodman and Royer inventions as set forth in claims 22, 26, 27 and 28 specified in paragraph 6 of the complaint.

The District Court in its opinion filed November 21, 1950 (App. 67) denied plaintiff's claim and on December 13, 1950 filed its Findings of Fact, Conclusions of Law and final Judgment (App 70-73) dismissing the complaint.

On January 10, 1951 appellant filed its notice of appeal in the District Court. The jurisdiction of this Court is based on 62 Stat. 929 (U. S. Code, Title 28, Section 1291).

II.

STATEMENT OF THE CASE.

(1) Introduction.

The Woodman and Royer patent application relates generally to the manufacture of the metal manganese by electrolytic processes. Manganese is a strategic and important metal in this nation's economy since every pound of steel embodies some manganese. (App. 45) The production of manganese by electrolytic processes makes possible the use of low grade ores available in this country. (App. 139)

Applicants' invention relates to the purification of a manganese salt solution such as a manganese sulphate solution prior to the use of the solution in the electro-deposition of manganese. After the manganese sulphate solution has been purified, it is placed in a tank or cell and an electric current is passed from one electrode, called an anode, to another electrode, called a cathode, to electrodeposit manganese on the cathode. The cathode is then removed from the cell and the manganese is stripped from it (App. 13, 14).

(2) The Woodman and Royer Invention.

The complete process for purifying a manganese salt solution as described in the Woodman et al. patent application is shown in Plaintiff's Exhibit 2 (App. 109) and is described in detail in the testimony of Woodman (App. 11 to 13). The principal features of the Woodman et al. process are shown more succinctly in Plaintiff's Exhibit 17, right-hand column (App. 153).

Referring to Plaintiff's Exhibit 2 (App. 109), Woodman in his testimony described the Woodman and Royer process as follows:

The manganese ore as mined is not suitable for leaching with sulphuric acid to form the manganese salt solution (App. 11). Accordingly, the manganese ore is subjected to a reducing roast or, in other words, it is thrown into a hot furnace and oxygen is taken away from it as indicated by step 1 of Exhibit 2. The reduced ore is then leached with sulphuric acid as shown in step 2 and ammonia is added for the purpose of aiding electro-deposition of manganese in a later step. The sulphuric acid leaches from the ore the manganese, thereby forming a manganese sulphate solution. The sulphuric acid also leaches from the ore impurities such as iron, arsenic, copper and nickel, so that the leach solution formed in step 2 contains manganese sulphate, ammonium sulphate and the impurities such as the sulphates of iron, arsenic, copper, nickel, etc.

After leaching, the ore is filtered from the solution in step 3 and the ore residue (4) is discarded as being worthless.

The solution from the filter in step 3 goes to what is called the iron purification, which is step 5. Here iron is added to the solution, providing not enough iron has been leached from the ore to carry down with it all of the arsenic, which has been leached from the ore. The solution is oxidized with air and this precipitates the iron which carries down with it the arsenic, provided a sufficient amount of iron is present. Additional iron is added if this amount is found to be insufficient. *This step does not precipitate the copper or nickel be-*

*cause the copper and nickel are present in the solution as sulphates (App. 12).**

The iron precipitate is filtered from the solution in step 6 and in step 7 the iron-arsenic impurities are discarded because they are worthless.

The solution from the filter 6 is passed to the hydrogen sulphide purification 8. Here the solution is treated with hydrogen sulphide to convert the *sulphates* of copper and nickel to *sulphides* of copper and nickel, some of which precipitate and are filtered off. However, copper and nickel sulphides are somewhat soluble in the solution so that the precipitation of copper and nickel sulphides is not complete and small amounts of copper and nickel sulphides remain dissolved in the solution. This solution is not suitable for the electrodepositing of manganese on a commercial scale (App. 13). This is so because of minute amounts of impurities remaining in the solution, impurities so minute that an analytical laboratory cannot detect them.

After the sulphide purification, the solution is again filtered in step 9 and the copper-nickel impurities, step 10, are discarded because they are worthless.

The solution then goes to the final purification which is step 11. Here, iron as ferrous sulphate, along with air, is added to the solution containing copper and nickel sulphides. Some of the ferrous sulphate will react with the copper sulphide and with the nickel sulphide to form iron-copper sulphide and iron-nickel sulphide. Such compounds are less soluble than the copper sulphide and nickel sulphide and therefore precipi-

* Throughout this brief, italics are ours unless the contrary is indicated.

tate. Any excess iron added here will be precipitated as an iron hydroxide.

The precipitate is then filtered off in step 12 and the solution 14 is fed to the manganese electrolytic cell 15.

The three principal steps of the Woodman et al. process are shown in Plaintiff's Exhibit 17 (right-hand column) (App. 153) and are as follows:

Step 1. Iron (as ferrous sulphate) is added to the manganese sulphate solution and the solution is oxidized with air. This precipitates the iron and arsenic which are filtered from the solution but does not remove the copper, nickel or cobalt impurities.

Step 2. The solution is treated with hydrogen sulphide which removes some of the nickel, cobalt and copper impurities but some of these impurities remain in solution.

Step 3. Ferrous sulphate is added to the solution from the sulphide treatment. This results in further purification by removing soluble metal sulphides such as copper, cobalt and nickel sulphides from the solution.

From the above it is seen that in applicants' process one of the essential steps is the addition of iron (usually as ferrous sulphate) to a solution which has been treated previously with a soluble sulphide such as hydrogen sulphide.

The two principal references relied on by the Patent Office are Hannay et al. patent 2,259,418 and Bureau of Mines Bulletin R. I. 3406.

(3) Hannay et al. Patent No. 2,259,418.

A copy of this patent was introduced in evidence in the District Court as Plaintiff's Exhibit 10 (App. 141-146). The Hannay process was described in detail by the witness Woodman (App. 33 to 38) in connection with Plaintiff's Exhibit 11 (App. 147).

The Hannay et al. patent (page 2, col. 1, lines 6-16) states:

"The solution obtained from the leaching step is filtered at 4 and the filtrate is purified to remove impurities such as nickel, cobalt, zinc, lead, iron, arsenic and antimony. While we do not wish to limit the scope of our present invention to any particular purification step, we have found that the use of hydrogen sulphide for the precipitation of metallic impurities present in solutions containing manganese is particularly suitable in this step of the process, *after removal of iron by standard methods.*"

The witness Woodman in describing the process of the Hannay et al. patent stated (App. 34) that in the leaching step 3 (Plaintiff's Exhibit 11) the manganese ore is leached with sulphuric acid and that the sulphuric acid leaches out the manganese and impurities such as cobalt, nickel, arsenic and iron. After the leaching step, Hannay filters in step 5 (Plaintiff's Exhibit 11) and then according to the portion of the Hannay et al. patent above quoted he says to remove iron by standard methods and *thereafter* to treat the solution with hydrogen sulphide. Woodman testified that the removal of iron "by standard methods" means either oxidation with air or with manganese dioxide (App. 34).

Thus the essential disclosure of the Hannay et al. patent is:

Step 1. Remove iron by oxidation with air or manganese dioxide.

Step 2. Thereafter, treat this solution with hydrogen sulphide.

(4) Bureau of Mines Bulletin R. I. 3406.

The process as described in Bureau of Mines Bulletin R.I. 3406 (Plaintiff's Exhibit 4; App. 111) was described in detail by the witness Woodman (App. 38 to 40) with the aid of Plaintiff's Exhibit 13 (App. 149). The essential steps of the Bureau of Mines process also are shown on Plaintiff's Exhibit 17, middle column, (App. 153). This process as described by Mr. Woodman in referring to Plaintiff's Exhibit 13 is as follows.

The manganese ore which has been calcined, i.e., subjected to a reducing roast, is taken from calcine storage 1 and fed to leaching tanks 2, where it is leached with sulphuric acid in order to leach out the manganese from the ore. In doing this, other impurities are leached out such as iron, arsenic, copper and nickel and since the acid used is sulphuric acid, the impurities present are *sulphates* of iron, arsenic, copper, nickel, etc.

The solution containing the impurities is filtered on filter 3 and the ore residue 4 is discarded as worthless.

In step 5 iron is added to the solution. This is done because according to the Bureau of Mines process a small amount of iron is added to the solution when the amount of iron present in the solution is not sufficient to carry

down the arsenic which has been leached from the ore. (App. 39) The iron, arsenic, copper, nickel, are all present in the solution as *sulphates*. When the iron is precipitated it carries down with it the arsenic. This step, however, does not precipitate the copper or nickel because they are present in the solution as *sulphates* and as such the iron has no effect on them (App. 39).

The iron and arsenic are filtered from the solution in step 6 and are discarded in step 7 because the precipitate is worthless.

The solution in step 8 is treated with xanthate, xanthate being a soluble sulphide, in order to convert the sulphates of nickel, copper, etc. into the sulphide form. In this form they precipitate and are removed from solution in filter No. 9. *However, some of those sulphides still remain in solution and are carried through the filter.* (App. 40)

The solution from filter No. 9 goes to the purified storage No. 11, where sulphur dioxide is added to the solution and the solution is then fed to the manganese electrolytic cell No. 12.

The essential steps of Bureau of Mines Bulletin R.I. 3406 are therefore—

Step 1. Addition of iron and oxidation with manganese dioxide to cause precipitation of iron and arsenic.

Step 2. Addition of xanthate (a soluble sulphide) to precipitate some of the cobalt and nickel.

The Patent Office also relied on the following Prescott & Johnson reference.

- (5) Prescott & Johnson "Qualitative Chemical Analysis", 5th Edition, Page 114 and 115.

This article (Plaintiff's Exhibit 16; App. 151, 152) relates to the precipitation or formation of arsenic sulphide when solutions containing arsenic are treated with hydrogen sulphide (App. 43). It is a text book reference giving directions for analyzing solutions in general but there is nothing in the article with regard to the purification of manganese solutions (App. 43). The article states, page 114, that hydrogen sulphide will not completely precipitate arsenic from its hydrochloric acid solution if (1) the solution is not completely saturated with hydrogen sulphide; (2) too much hydrochloric acid is present; (3) the solution contains much pentad arsenic. (Finding of Fact No. 6; App. 71).

III.

STATEMENT OF POINTS.

1. The Patent Office and the District Court erred in failing to take into consideration the fact that applicants' process involves a combination of steps in a certain sequence, which sequence of steps is critical and essential for obtaining the desired results.

2. The Patent Office and the District Court erred in holding that applicants' process is obvious in view of the references cited by the Patent Office when there is no suggestion in the references that they should be combined or how to combine them.

3. The Patent Office and the District Court erred in holding that applicants' process was obvious when in fact the need for the invention had existed for many years and prior attempts by those skilled in the art to solve the problem had resulted in failure.

4. The Patent Office and the District Court erred in failing to give due weight to the commercial success of applicants' invention.

5. The Patent Office Tribunals and the District Court erred on material factual matters.

6. The Patent Office and the District Court erred in holding that there is a departure between the *theories* expressed in the Woodman and Royer application and those expressed by Woodman at the trial.

7. The Patent Office and the District Court erred in failing to hold that it is immaterial whether any *theory* is expressed in a patent application and in failing to hold that an inventor need not understand the scientific principles underlying his invention.

IV.

SUMMARY OF ARGUMENT.

1. Applicants' process involves a combination of steps in certain sequence, which sequence of steps is critical and essential for obtaining the desired results. Applicants' first principal step is the treatment of the manganese solution with iron (ferrous sulphate for example) and oxidation of the solution to precipitate iron and arsenic. (App. 12) Applicants' second principal step is the treatment of the solution with hydrogen sulphide or other soluble sulphide to convert the impurities such as copper and nickel sulphates into copper and nickel sulphides. (App. 12) Applicants' third principal step is to treat with ferrous sulphate, the solution in which the impurities are present as sulphides. (App. 13) In order to remove copper and nickel impurities it is essential that the ferrous sulphate treatment follow a treatment which converts these impurities from the sulphate form to the sulphide form. (App. 14, 15)

2. The Hannay et al. patent No. 2,259,418 discloses merely the removal of iron by oxidation followed by treatment with hydrogen sulphide. It does not disclose the step of treating a manganese solution with a metallic salt such as ferrous sulphate after treatment of the solution with hydrogen sulphide (App. 36).

3 and 4. The Bureau of Mines Bulletin R.I. 3406 describes only the addition of ferrous sulphate to a manganese solution as the first step of a purification process and only for the purpose of removing iron and arsenic. (App. 39) It does not disclose addition of

ferrous sulphate to a manganese salt solution which has been previously treated with hydrogen sulphide to convert the impurities into the sulphide form and it does not accomplish the same result as is accomplished by applicants' invention. (App. 40, 41)

5. (a) The fact that Woodman and others skilled in the art failed in their prior attempts to solve the problem shows that applicants' combination and sequence of steps was not obvious to one skilled in the art. While Woodman was in the Research Department of the Anaconda Copper Mining Company during the period 1935-40 (App. 17-20), he and others skilled in the art worked for fifteen months on the problem of purifying solutions to be used in the electrolytic deposition of manganese but after fifteen months of research, the Anaconda Company dropped the investigation for the reason that it was not considered commercially feasible (App. 18). During this investigation at Anaconda it did not occur to Woodman or to any of the other experts that the problem could be solved by treating the manganese solution with ferrous sulphate after a previous hydrogen sulphide treatment which converts the impurities from the sulphate form to the sulphide form.

After Woodman went with the Bureau of Mines in December, 1940 he and Royer worked on the problem unsuccessfully for a further period of four or five months before they made the invention. (App. 23) *Prior to the adoption of the Woodman and Royer invention, the result obtained was a commercial failure. The invention made the difference between success and failure and it was not until after the adoption of the in-*

vention that results which were consistent and satisfactory were obtained. (App. 23, 65)

(b) The adoption by the Bureau of Mines of the Woodman and Royer invention gave results which were greatly superior to those obtained previously (App. 23). It gave consistent results and much higher current efficiency (App. 26-27).

(c) The commercial success of the Woodman and Royer invention is shown by Plaintiff's Exhibit 6 (App. 127), Exhibit 7 (App. 137), Exhibit 8 (App. 139), and in the testimony of Woodman (App. 29-32). By February, 1944 more than one-half million pounds of electrolytic manganese had been produced according to the Woodman and Royer invention, by October, 1944 more than one million pounds of electrolytic manganese had been produced and by October, 1946 the production of electrolytic manganese had exceeded one and one-half million pounds.

6. The Commissioner's contention that the Woodman and Royer invention is obvious is based on assumptions not supported by the record. One such assumption is that after their hydrogen sulphide treatment, the inventors believed that it was the presence of the impurity arsenic which prevented successful electrodeposition and that their purpose in adding ferrous sulphate after a hydrogen sulphide treatment was to remove arsenic. This assumption is wrong. Woodman testified (App. 52) that the inventors had no reason to believe that it was arsenic which was giving the trouble. He stated that arsenic was the farthest thing from their minds.

7. The Patent Office Tribunals and the District Court erred on material factual matters. The Patent

vention that results which were consistent and satisfactory were obtained. (App. 23, 65)

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7. The Patent Office Tribunals and the District Court erred on material factual matters. The Patent

Office Board of Appeals in its decision (App. 100) held that if the manganese solution to be purified initially contained insufficient iron to effect proper precipitation of impurities more iron could be added without invention. Factually this is incorrect. The evidence shows that if more iron were added initially it would have no effect on the removal of copper, nickel, cobalt and the like impurities (App. 15, 43 and 48).

8. (a) The opinion of the District Court (App. 68) holds that there is departure between the theories expressed in the Woodman and Royer application and those expressed by Woodman at the trial. There actually is no departure. The specification when taken as a whole, shows that the inventors did not know the theory or scientific principles which made the process a success but that they did know and did disclose the actual steps which should be employed. They knew furthermore that they could take a solution made by the Bureau of Mines procedure but which would not electrodeposit manganese, treat that solution according to their invention, and it would deposit manganese very satisfactorily.

Even if there were a departure between the theories given in the application and those expressed by Woodman at the trial, it would be immaterial because an inventor is not required to explain the theories or scientific principles on which his invention is based and in fact he need not even disclose the theories or scientific principles. It is only necessary that he disclose an operative process which one skilled in the art can follow and accomplish the desired results.

V.

ARGUMENT.

(1) The Sequence of Steps in the Woodman and Royer Process Is Critical.

Applicants' process involved a combination of a series of steps in a *certain sequence*, which sequence of steps is critical and essential for obtaining the desired results. Applicants' first step is the treatment of the manganese solution with iron (ferrous sulphate for example) and oxidation of the solution, thereby causing the precipitation of iron which carries down with it the arsenic. This step does not precipitate the copper or nickel because the copper and nickel are present in the solution at this stage of the process as sulphates (App. 12).

Applicants' second step is the treatment of the solution with hydrogen sulphide or other soluble sulphide. This precipitates some of the copper and nickel sulphides but this precipitation is not complete because some of the copper and nickel sulphides remain dissolved in the solution. This solution is not suitable for the electrodepositing of manganese on a commercial scale (App. 13).

According to applicants' third step, the solution is treated with ferrous sulphate along with air. Some of the ferrous sulphate reacts with the copper sulphide in solution and with the nickel sulphide in solution to form iron-copper sulphide and iron-nickel sulphide and since such compounds are less soluble than copper sulphide and nickel sulphide, they precipitate and are removed from the solution.

It is abundantly clear from the testimony of Woodman that the sequence of using these steps is critical and that you will not get satisfactory results unless they are used in the order specified. Woodman was asked (App. 14) to tell why it is that the addition of ferrous sulphate in step 5 as set forth on Plaintiff's Exhibit 2 does not precipitate out or eliminate the copper or nickel so that these impurities can be removed, whereas at a later time in the process, namely, *after the hydrogen sulphide treatment*, the addition of the ferrous sulphate in step 11 does serve to precipitate out the nickel, cobalt and copper impurities that are in the solution. His answer was:

"The iron in Step (5) comes from the ore, or can be added. In any event, it is added to a solution where all of the metals are present as *sulphates* and iron addition is *at this stage* of absolutely no effect on removing nickel, cobalt from the solution, whereas in Step (11) after the sulphide purification, those metals are present there as the *sulphides* and when they are present as the sulphides, the addition of iron will remove those sulphides from solution." (App. 14, 15)

He also was asked the following question (App. 15):

"Then, as I understand it, when these impurities are in the *sulphate* form as they are up in Step (5), the treatment with ferrous sulphate will not remove them and it is not until after you convert the sulphates to *sulphides* that a ferrous sulphate treatment will remove those impurities, is that it?"

and replied:

"That is correct."

Mr. Woodman further testified (App. 48) "The sequence of those steps is the critical part of the invention" in referring to the second and third steps of the

Woodman et al. process as shown on Plaintiff's Exhibit 17 (right hand column; App. 153).

He was asked the question (App. 48):

"Now, in your testimony, you have emphasized the fact that your ferrous sulphate treatment follows after a hydrogen sulphide treatment of the solution. Is that a matter of importance that that step follow after the hydrogen sulphide treatment?" He answered:

"Yes, that is the important step, it is the critical step in the process."

(2) The Hannay et al. Patent No. 2,259,418 Does Not Disclose the Invention.

The Hannay et al. patent discloses merely the removal of iron by oxidation followed by treatment with hydrogen sulphide. As stated on page 1 of "Defendant's Reply to Brief for Plaintiff," filed in the District Court, October 25, 1950 (not printed):

"The Hannay et al patent was cited merely to establish the conventionality of the preliminary treatment, including the use of a sulphide, and its effectiveness as a reference in this connection has not been questioned."

The process of the Hannay et al. patent has not gone into commercial use (App. 35) and it does not disclose the step of treating a manganese solution with a metallic salt, such as ferrous sulphate, *after treatment of the solution with hydrogen sulphide* (App. 36).

(3) The Bureau of Mines Bulletin R. I. 3406 Does Not Disclose the Invention.

This bulletin does not disclose the essential step of applicant's process which is the addition of ferrous sulphate or other similar salt to a manganese salt solution *which has been previously treated with a soluble sulphide such as hydrogen sulphide to convert the impurities into the sulphides*. It describes only the addition of ferrous sulphate to a manganese solution as the first step of a purification process and only for the purpose of removing iron and arsenic. The addition of ferrous sulphate at this stage, although effective for the removal of iron and arsenic, has no effect on the removal of copper, cobalt or nickel. (App. 39)

(4) The Addition of Ferrous Sulphate to a Solution in which the Impurities are Present as Sulphides is not Disclosed by the Prior Art.

The only reference relied on by the Patent Office which discloses the addition of ferrous sulphate to a manganese solution is the Bureau of Mines Bulletin R. I. 3406. In the process there described the ferrous sulphate is added to a leach solution made by leaching the calcined ore with sulphuric acid. Accordingly, as testified by Woodman (App. 39), the impurities cobalt, copper and nickel are in the solution in the form of *sulphates* and the addition of ferrous sulphate has no effect in precipitating them.

The Solicitor of the Patent Office argues that according to the Bureau of Mines Bulletin R.I. 3406 there is a general statement on page 7 with respect to arsenic

which teaches that the ferrous sulphate can be added to the solution at any time and that the ferrous sulphate addition does not necessarily precede the xanthate treatment. Woodman on direct examination (App. 48-50) testified that the sequence of steps disclosed in this Bulletin is to first treat the solution with ferrous sulphate and then with xanthate. He testified that this sequence is shown in the flow sheet Figure 2 (App. 114) and described on pages 8 and 9 of the Bulletin under the heading "A Purification Batch." (App. 116 and 117). He said (App. 49) "They make no suggestion about altering that sequence of operation." See also Woodman's testimony on cross examination to the same effect (App. 61). He pointed out (App. 41) that the essential difference between the process of R.I. 3406 and the Woodman and Royer process is that Woodman and Royer add iron *after* the sulphide treatment, whereas the Bureau of Mines process adds iron *before* the sulphide (xanthate) treatment.

(5) Applicants' Combination and Sequence of Steps is not Obvious to One Skilled in the Art.

Applicants' sequence of steps is:

(1) Treating the solution with ferrous sulphate and oxidizing to remove iron and arsenic.

(2) Treating the solution with a soluble sulphide.

(3) Treating the solution with ferrous sulphate to remove cobalt, copper and nickel which have been previously converted from the sulphates to the sulphides.

The unobviousness of applicants' process to one skilled in the art is shown by the following facts, all of which stand uncontroverted.

- (a) *The failure of those skilled in the art to solve the problem.*

Woodman testified (App. 17, 18) that while he was in the research department of Anaconda Copper Mining Company in 1935-40 (App. 35) he worked for 15 months on the problem of purification of solutions to be used in the electrolytic deposition of manganese. When he was assigned the job of investigating the electrolytic manganese problem, the Anaconda Company sent him to Rolla, Missouri, at the Bureau of Mines Station, where he studied for approximately 2 weeks under Mr. S. M. Shelton, studying ore reduction, leaching, purification and deposition of manganese before he went back with the Anaconda Company to pursue the work there. *The Mr. Shelton with whom he studied at the Bureau of Mines is the same Mr. Shelton who is one of the authors of the Bureau of Mines Bulletin R. I. 3406.*

Mr. Woodman then set up a research laboratory electrolytic manganese plant and worked on such process for about 15 months before the company came to the conclusion that the process was not a commercial operation. *Thereupon the Anaconda Copper Mining Company dropped the investigation (App. 18). The process that Woodman and his associates used at Anaconda Copper Mining Company was the same process as described to him by Mr. Shelton in Rolla, Missouri, and was the same as that described in the Bureau of Mines Bulletin R. I. 3406 (App. 18). The process used by Woodman and others at Anaconda consisted of, first, oxidizing the iron; this removed the iron and carried down with it the arsenic that was leached from the ore. This solution was then filtered from the iron residue and was treated*

with xanthates according to the recommended Bureau of Mines procedure in R. I. 3406.

Others skilled in the art were working with Woodman at Anaconda. Mr. Woodman reported daily to Mr. Frick, the research director of the Anaconda Company (App. 19), but it did not occur to either Woodman or Frick to use the combination and sequence of steps claimed in the Woodman and Royer application. Mr. Frick was an expert in the field of electro-deposition. He was one of the originators of the electrolytic zinc process for the Anaconda Copper Mining Company developed around the years 1916-1918 and he also put up plants in South America and in Poland for the company (App. 20). Woodman told Mr. Frick of the difficulties which he was encountering but Frick did not make any worth while suggestions which would enable him to successfully solve the problem and the process was abandoned by Anaconda Copper Mining Company after a period of investigation which lasted about 15 months. The fact that Mr. Frick was an expert in the electrolytic zinc process which had been developed by Anaconda Copper Mining Company is important because methods for purification developed in the electrolytic zinc industry are applicable, with certain modifications, to the purification of manganese sulphate solutions. This is so stated in lines 2-5, page 7, of Bureau of Mines Bulletin R. I. 3406 (App. 115). Accordingly, Mr. Frick's long experience with the electrodeposition of zinc should have led him to solve the problem of purifying manganese solutions which were to be used in the electrodeposition of manganese if, in fact, the Woodman and Royer process was an obvious one.

The skilled workers at the Bureau of Mines had been working on the problem of a commercially satisfactory method of electrodepositing manganese, involving the purification of manganese solutions, since about 1936 (App. 8). Woodman went with the Bureau of Mines in December 1940. At that time the Bureau of Mines had abandoned the xanthates purification as described in their Bulletin R. I. 3406 and had substituted for that the use of hydrogen sulphide. Otherwise the procedure was the same as that described in R. I. 3406 (App. 21). At the Bureau of Mines Mr. Woodman worked under Dr. Koster, who was supervising engineer at the Boulder City, Nevada station, Dr. Koster being one of the originators in the Bureau of Mines of the electrolytic manganese investigation. Miles W. Royer also worked for Dr. Koster (App. 22). Dr. Dean was the chief engineer of the Western Metallurgical Division and was the superior of Dr. Koster. All of these men, Dr. Dean, Dr. Koster, Mr. Royer, were familiar with the work that was being carried on by the Bureau of Mines at Boulder City (App. 22). In addition, Mr. Crowell, Mr. Parkman, Mr. Hunter and Mr. Jacobs, all skilled technical men, were associated with Woodman and Royer in the work that they were doing at Boulder City in 1940 and 1941. All of these men were familiar with the work as it progressed but none of them made any suggestion to Mr. Woodman in regard to the use of a metallic salt such as ferrous sulphate for the purification of a manganese solution subsequent to a treatment with a xanthate or with hydrogen sulphide (App. 22).

In addition to the 15 months which Woodman and others spent in investigating the process while he was at Anaconda Copper Mining Company during 1935-40,

Woodman and Royer worked on the problem at the Bureau of Mines for a period of 4 to 5 months during 1940 and 1941 before they made the invention covered by the application here involved (App. 23).

The existence of a problem and the failure to solve it in spite of the need for its solution has always been considered strong evidence of patentability. The case of *Kelley et al. v. Coe*, (C.A. D.C. 1938) 99 F.2d, 435 is particularly pertinent to the present situation. In that decision it was stated page 442:

"The Commissioner's argument in the present case comes down to the same result. He contends that anyone skilled in the art could have taken this and that from the various patents and, putting them together, could have devised the Kelley method. But the fact remains that, in the face of a crying need for a new process or method in the industry, not one of the best engineers in the world, with their attention especially directed to the subject for approximately thirty years, was able to see what Kelley saw, or to produce the result which he produced. The evidence in support of appellants' application establishes beyond doubt their right to the issuance of a patent."

In the present case the Commissioner contends that anyone skilled in the art could have taken the Hannay et al. patent No. 2,259,418, the Bureau of Mines Bulletin R.I. 3406 and the Prescott and Johnson reference and by putting them together could have devised the Woodman and Royer invention. But the fact remains that the skilled workers at the Bureau of Mines had been working on the problem since about 1936 and it was not until 1941 that Woodman and Royer solved it.

In the *Kelley* case the decision states page 441:

"Kelley himself first worked on the theory of the prior art and failed. It was only when he used the particular combination described in his claims that he succeeded."

So also here, Woodman while at Anaconda Copper Mining Company in the years 1935-40 used the exact process described in Bureau of Mines Bulletin R.I. 3406 and yet his company abandoned the process as not being commercially satisfactory after Woodman and others had spent fifteen months in investigating the process. It was not until after Woodman and Royer used the last step of their process, i.e., the addition of ferrous sulphate to a solution which had previously been treated by hydrogen sulphide that they succeeded. The fact that this last step may seem simple now that the method has been disclosed does not disprove invention. In the *Kelley* case the decision states page 440:

"The fact that Kelley's method may seem simple in its operation does not disprove invention. The difference between it and the prior art may not be great in a physical sense, but slight as it may seem to be it was sufficient to achieve success where success had never before been achieved. It was not merely one step in a developmental process, but was the one step from failure to success. As was said in *The Barbed Wire Patent*, 143 U.S. 275, 282-283:

'Under such circumstances courts have not been reluctant to sustain a patent to the man who has taken the final step which has turned a failure into a success. In the law of patents it is the last step that wins. * * * There are many instances in the reported decisions of this court where a monopoly has been sustained in favor of the last of a series of inventors, all of whom were groping to attain a certain result, which only the last one of the number seemed able to grasp.'

Diamond Rubber Company of New York v. Consolidated Rubber Tire Company, (U. S. Supreme Ct., 1911), 220 U.S. 428, 434-435:

"Many things, and the patent law abounds in illustrations, seem obvious after they have been done, and, 'in the light of the accomplished result,' it is often a matter of wonder how they so long 'eluded the search of the discoverer and set at defiance the speculations of inventive genius.' *Pearl v. Ocean Mills*, 11 Off. Gaz. 2. Knowledge after the event is always easy, and problems once solved present no difficulties, indeed, may be represented as never having had any, and expert witnesses may be brought forward to show that the new thing which seemed to have eluded the search of the world was always ready at hand and easy to be seen by a merely skillful attention. But the law has other tests of the invention than subtle conjectures of what might have been seen and yet was not. It regards a change as evidence of novelty, the acceptance and utility of change as a further evidence, even as demonstration."

In *Wach v. Coe*, 77 F. 2d 113, 64 App. D.C. 235 it was held, page 115:

"Where, as here, the new device is also useful and marks a distinct and novel advance in the art, it should receive patent protection. For almost 25 years, as we have seen, patents have been granted in this art on devices that proved to be practically worthless, and yet appellant has been refused a patent on his successful device because the Patent Office has found that, by taking this and that from the unsuccessful patents, the result achieved by appellant could have been accomplished."

Even if each of the steps of applicants' process was old in the art (which is not the case here) it would not preclude invention. In *Universal Products Co., Inc. et al. v. Coe, Commissioner of Patents*, (D.C. D.C. 1940) 34 F. Supp. 372, the opinion states, p. 373:

"There is no novelty in these elements. Prior to the disclosure of the claims here being considered, however, there was no combination of these four elements, and I am convinced that, until they were brought into combination, the elements could not produce the results which, in the association into which Warner brought them, they did produce."

In the present case the successful results are not accomplished until the various steps are brought together in the sequence taught by the applicants. The treatment of the solution with ferrous sulphate must follow a prior treatment of the solution with a soluble sulphide such as hydrogen sulphide.

Where a demand has long existed and men skilled in the art have sought to meet that demand without success, the argument that the methods employed by the inventor who has solved the problem are so obvious as to involve only mechanical skill, is not entitled to very serious consideration.

Inland Mfg. Co. v. American Wood Rim Co., (C.C.A. 6, 1926), 14 F. 2d 657, 659:

"It is no argument against invention that the inventor availed himself of all knowledge known to mechanics skilled in the art, nor is it surprising that, when a definite result has been accomplished, the simplicity of the methods by which it is accomplished would seem to be obvious. The line between the skilled mechanic and the ingenuity of the inventor cannot be accurately drawn in any given case, but where a demand has long existed, and men skilled in the art have sought to meet that demand without success, the argument that the methods employed by the inventor who has solved the problem are so obvious as to involve only mechanical skill, is not entitled to very serious con-

sideration. *Diamond Co. v. Consolidated Tire Co.*, supra; *Consolidated Brake-Shoe Co. et al. v. Detroit Steel & Spring Co. et al.* (C.C.) 59 F. 902, 908; *Star Brass Works v. General Electric* (C.C.A. 6) 111 F. 398, 400, 49 C.C.A. 409; *American Ball Bearing Co. v. Finch* (C.C.A. 6) 239 F. 885, 889, 153 C.C.A. 13."

Paramount Publix Corp. v. American Tri-Ergon Corp., (U. S. Sup. Ct., 1935), 294 U.S. 464, 474:

"Where the method or device satisfies an old and recognized want, invention is to be inferred, rather than the exercise of mechanical skill. For mere skill of the art would normally have been called into action by the generally known want. See *Loom Co. v. Higgins*, 105 U.S. 580, 591; *Krementz v. Cottle Co.*, 148 U.S. 556, 560; *Hobbs v. Beach*, 180 U.S. 383, 392; *Carnegie Steel Co. v. Cambria Iron Co.*, 185 U.S. 403, 429, 430; *Expanded Metal Co. v. Bradford*, 214 U.S. 366, 381."

National Tube Company v. Steel & Tubes, Inc., (C.C.A. 3, 1937), 90 F. 2d 52, 57:

"It may be true that an expert, after Belmont had made his contribution to the art, might go to the art and select one thing from one patent and another thing from another patent and from many bring together a combination which would produce the result achieved by Belmont. So could it be done in almost every other patent except purely pioneer patents, but the Belmont patent described a new combination of old elements which produced a new result and is valid."

National Hollow Brake-Beam Co. et al. v. Interchangeable Brake-Beam Co., 106 Fed. 693, 706-707, (C.C.A. 8, 1901):

"The second claim of the first patent to Hien is for a combination of old mechanical elements in a new way. It is not for new elements, but for a new method of combining old elements; and a new combination of old elements, whereby a new and

useful result is produced, or an old result is attained in a more facile, economical, and efficient way, may be protected by patent as securely as a new machine or composition of matter."

The Commissioner's contention is that it would be obvious to combine the teachings of the Hannay et al. patent, the Bureau of Mines Bulletin R.I. 3406 and the Prescott and Johnson article. But in order for a combination of references to be proper, it is necessary that one of the references show the general combination. The general combination claimed by applicants is the treatment with a soluble sulphide such as hydrogen sulphide followed by a treatment with ferrous sulphate. No single reference cited by the Patent Office shows this general combination nor is there any suggestions in any of the references that they should be combined in the manner suggested by the Patent Office tribunals. In *Ex Parte Gee*, 1919 C.D. 49, 50, 51, (1919), it was held:

"The applicant's defined structure is new, and it seems to me that in order to negative invention it is necessary to find in the prior art not merely a device which might be modified to make this construction, *but somewhere a suggestion not only that the modification ought to be made but how to make it.*"

In order to properly combine patents in anticipation of a combination claim, it is indispensable that all of the elements of the claim or their mechanical equivalents be found in one reference where they do substantially the same work by the same means as is done by the elements in the combination claim.

Ottumwa Box Car Loader Co. v. Christy Box Car Loader Co., 215 Fed. 362, 369, (C.C.A. 8, 1914):

"It constitutes no anticipation and no defense to a claim of infringement that one or more elements of a patented combination, or one or more parts of a patented improvement, may be found in one old patent or publication, and others in another, and still others in a third. *It is indispensable that all of them, or their mechanical equivalents, be found in the same description or machine, where they do substantially the same work by the same means.*"

In the present case no single reference discloses applicants' combination of steps. In applicants' process the use of ferrous sulphate following the treatment with hydrogen sulphide is for the purpose of removing copper, cobalt and nickel impurities. The Bureau of Mines Bulletin R.I. 3406 teaches using ferrous sulphate prior to xanthate treatment for the purpose of removing arsenic which is a different purpose than removing copper, cobalt and nickel.

In *Ex Parte Worden*, 77 USPQ 667, 668-669, Patent Office Board of Appeals (1947), it was held:

"It is our view that the examiner has improperly combined the Niks and Kolitsch patents, since the suggestion for placing the blast pipe of Kolitsch at the point claimed by appellant is only found in appellant's disclosure."

In the present case there is no suggestion in any of the references for using the ferrous sulphate treatment of the Bureau of Mines Bulletin R.I. 3406 after a hydrogen sulphide treatment.

In *Ex Parte Arens*, 52 USPQ 551, 552, Patent Office Board of Appeals (1942), the opinion states:

"Moreover, we do not feel that it would be proper to combine Gilman with Arens as there is

nothing in either patent suggestive of the combination. In other words, neither patent shows a combination which even broadly responds to that here claimed."

(b) *Improved Results Obtained by the Woodman and Royer Process.*

The results obtained according to the Woodman and Royer process were greatly superior to those obtained according to the Bureau of Mines process described in R. I. 3406 or in that process when modified by the substitution of hydrogen sulphide for xanthates. Woodman testified (App. 23) :

"The result that we had obtained prior to the time of the invention, as far as a commercial unit is concerned, was an absolute failure. Upon the advent of this invention, we found that we could plate solutions satisfactorily and continuously, therefore, it meant the difference between failure and a good operating plant."

He further testified (App. 24) that before the Woodman and Royer invention they could plate for a few hours at a time but they never knew from one purification batch to another whether the solution would plate. After the invention they could plate with certainty, whereas prior to the making of the invention they did not have a degree of certainty which would have been satisfactory for any commercial operation. Many times they took the solution made according to the old process after the hydrogen sulphide precipitation step and tried to plate the solution but it would not plate. They then gave it the iron treatment of the Woodman and Royer process and found that they could plate and deposit the manganese from the solution very satisfactorily.

The witness Parkman testified (App. 65) :

"The electrodeposition of manganese prior to the adoption of the Woodman and Royer process, was most discouraging. We obtained no consistent results. We had no assurance that any solution would work. We did for a short time, of course, obtain deposits, but with no consistency from one batch of solution to another. It was not until the adoption of the Woodman-Royer process that we obtained results that were consistent and satisfactory."

They found that the adoption of the new process gave higher current efficiencies. By "current efficiency" is meant the amount of manganese that is actually deposited as against the amount of manganese that should theoretically be deposited for a given amount of electrical current passed through the solution in the electrodeposition of manganese (App. 25).

Before the adoption of the Woodman and Royer invention the current efficiencies were very low. One never knew what current efficiencies you were going to obtain, in some cases they were nil and sometimes the current efficiencies were up to 50%. After the adoption of the Woodman and Royer invention the current efficiencies ran from an average of 50 up to as high as 60 or 65% over a 24 hour period, the current efficiencies being on the average about 55 or 56%. Under optimum conditions an average current efficiency of 65% was obtained over a 24 hour period (App. 26, 27).

The question of current efficiency is a very important factor because the number of pounds of electrolytic manganese that a plant will produce in a day depends upon it. (App. 28)

(c) *Commercial Success of the Woodman and Royer Process.*

The article "First Two Years Operation of the Bureau of Mines Electrolytic Manganese Pilot Plant at Boulder City, Nevada" by J. H. Jacobs et al. (Plaintiff's Exhibit 6; App. 127) was published in Feb. 1944. In referring to this exhibit Woodman testified (App. 30) that this publication showed that the Pilot Plant operations were begun in November 1941 and that at the time of the publication (February 1944) more than one-half million pounds of manganese had been produced. The statement at the top of page 410, first column, of Exhibit 6 (App. 129) — "It was found that if 0.1 gram of iron per liter of solution was added as copperas and the solution was oxidized with air and filtered, all of the aforementioned materials were removed" deals with the Woodman and Royer process. The authors of the process described in Exhibit 6 in referring to the Woodman and Royer process state: "This was an important improvement because it always insured a pure solution for electrolysis." (App. 30).

Woodman testified (App. 31) with respect to Plaintiff's Exhibit 7 (App. 137), which is a publication entitled "The Effect of Certain Variables on the Electrodeposition of Manganese" by J. H. Jacobs et al. That publication, which was published in October 1944, shows that more than 1 million pounds of manganese metal had been produced. Woodman testified that the word "copperas" used in this publication is another name for ferrous sulphate (App. 31).

Woodman also testified (App. 32) with respect to Plaintiff's Exhibit 8 (App. 139), which is a publication

by J. H. Jacobs entitled "The Effect of Cell Variables on the Electrowinning of Manganese" published in October 1946. This publication, page 439, states that the Bureau of Mines had been carrying out research and development work on a process for the electrowinning of manganese from low grade ores for the past 10 years, showing that such work was begun by the Bureau of Mines in 1936. The publication shows (page 440) that more than 1½ million pounds of manganese metal had been produced by that time according to the Woodman and Royer invention.

(6) The Commissioner's Contention that the Woodman and Royer Invention is Obvious is Based on Assumptions not Supported by the Record.

The Commissioner's argument that applicants' process is obvious is briefly as follows:

(a) Applicants' first two steps of oxidizing the solution to precipitate iron and then treating with hydrogen sulphide is disclosed in Hannay et al. patent No. 2,259,418.

(b) Applicants' purpose in adding ferrous sulphate following the hydrogen sulphide treatment was to remove arsenic.

(c) The Prescott and Johnson reference shows that treatment of a solution with hydrogen sulphide will not precipitate all of the arsenic.

(d) Therefore, in view of Bureau of Mines Bulletin R.I. 3406, it was obvious to add on to the Hannay disclosure the step of adding ferrous sulphate after the treatment with hydrogen sulphide for the purpose of removing arsenic which had not been removed by the hydrogen sulphide treatment.

Referring to (a) above, we admit that the Hannay patent discloses the first two steps of the Woodman and Royer process as given in Exhibit 17, right-hand column, (App. 153).

Referring to (b) above, since the purpose of the Bureau of Mines addition of ferrous sulphate *before* a hydrogen sulphide treatment is to remove arsenic, it would not be obvious to add ferrous sulphate *after* a hydrogen sulphide treatment unless the purpose also was to remove arsenic. The fact is that where applicants add ferrous sulphate after a hydrogen sulphide treatment, the result accomplished is entirely different than if the ferrous sulphate were added before the hydrogen sulphide treatment. Addition of ferrous sulphate prior to the hydrogen sulphide treatment will remove arsenic but will not remove copper, nickel or cobalt. However, where ferrous sulphate is added following a treatment with hydrogen sulphide so that the cobalt, copper and nickel *sulphates* have been converted into the *sulphides*, the addition of the ferrous sulphate will precipitate and remove these *sulphides* from the solution. Woodman testified (App. 14) in referring to Plaintiff's Exhibit 2 (App. 109):

"The iron in Step (5) comes from the ore, or can be added. In any event, it is added to a solution where all of the metals are present as *sulphates* and iron addition is at this stage of absolutely no effect on removing nickel-cobalt from the solution, whereas in Step (11) after the sulphide purification, those metals are present there as the *sulphides* and when they are present as the sulphides, the addition of iron will remove those sulphides from solution."

In carrying out the Woodman and Royer process, after the solution had been treated with hydrogen sul-

phide there was no reason to believe that the solution would contain arsenic in any amount which would prevent satisfactory electrodeposition of the manganese. The Solicitor of the Patent Office in cross-examining Mr. Woodman tried to prove that at the time of making the Woodman and Royer invention, Mr. Woodman believed that the reason that the solution would not plate satisfactorily after the hydrogen sulphide treatment was because it contained arsenic. In answer to the question by the Solicitor "You had some reason to believe that there might be arsenic in there, didn't you?" (App. 52), Mr. Woodman answered:

"I had no reason, in fact, the fact of the matter is all through the years of electrolytic zinc plant operations and all, the first step where we add ferrous sulphate to remove arsenic has always proven very successful. *We had no reason to believe it was arsenic. In fact, arsenic was the farthest thing from our minds.*"

Referring to (c) above, the Patent Office Solicitor in his brief in this Patent Office entitled "Defendant's Reply to Brief for Plaintiff" (not printed) beginning at the bottom of page 4, states:

"Moreover, it should be noted that the sulphide treatment, either following an iron sulphate step or used without such a step, would not eliminate all arsenic. This is established by the section of the Prescott and Johnson Book referred to at the trial (transcript, page 18, second full paragraph) and, more effectively, by the plaintiff's exhibits 6, 7, and 8 which note that one of the purposes of the plaintiff's process is the removal of residual arsenic after sulphide treatment."

These statements are without any foundation in the testimony. The Prescott and Johnson reference states nothing in regard to the purification of manganese solu-

tions. It relates merely to the precipitation or formation of arsenic sulphide when solutions containing arsenic are treated with hydrogen sulphide (App. 43). The disclosure of the Prescott and Johnson reference is correctly stated in Finding of Fact No. 6 of the District Court's Findings of Fact which reads (App. 71) :

" 'Quantitative Chemical Analysis' by Prescott and Johnson, on pages 114 and 115, states that the hydrogen sulphide will not completely precipitate arsenic from its hydrochloric acid solution if (1) the solution is not completely saturated with hydrogen sulphide; (2) too much hydrochloric acid is present; (3) the solution contains much pentad arsenic."

Such Finding of Fact means, in effect, that the Prescott and Johnson disclosure is that if you want to precipitate substantially all of the arsenic you must carry out the method in a proper manner. Every process for accomplishing every result must be carried out in a proper manner. It is clear from the evidence that in carrying out the Woodman and Royer process the hydrogen sulphide treatment was carried out in a proper manner and in such manner as to remove substantially all of the arsenic. Mr. Woodman was asked the question (App. 52) :

"You were familiar with the material stated in the Prescott and Johnson book to the effect that hydrogen sulphide treatment would not necessarily remove all the arsenic?"

Mr. Woodman answered:

"According to that article, on certain solutions performed in certain ways, not according to the way that we worked our sulphide purification, it may be possible that arsenic might not be precipitated by the sulphide treatment. *But here is the point, we removed arsenic thoroughly before the sulphide*

treatment, therefore, the article in Prescott and Johnson has no significance to our invention."

The contention made by the Solicitor that Plaintiff's Exhibits 6, 7 and 8 (App. 127, 137 and 139) establish that an iron sulphate treatment followed by a hydrogen sulphide treatment would not eliminate all the arsenic is clearly erroneous. Woodman pointed out (App. 54) that in the processes of Exhibits 6, 7 and 8 the step of adding ferrous sulphate prior to a hydrogen sulphide treatment in order to remove arsenic is eliminated. Therefore, these publications do not show that if you first add ferrous sulphate to remove iron and arsenic and then treat the solution with hydrogen sulphide you will not remove all of the arsenic, as contended by the Solicitor.

(7) The Patent Office Tribunals and the District Court Erred on Material Factual Matters.

Entirely apart from the lack of complete knowledge on the part of the Patent Office of the historical background of the invention, which refutes the main ground of rejection, the Patent Office erred on other material facts.

(a) The Patent Office Examiner in his statement before the Board of Appeals (App. 85) and the Patent Office Board of Appeals in its decision (App. 100) held that if the manganese solution to be purified initially contained insufficient iron to effect proper precipitation of impurities, more iron could be added without invention. Factually this is incorrect. The evidence shows that if more iron were added initially, it would have no effect on the removal of the copper, nickel, cobalt and the like and that in order to eliminate these impurities,

the solution must be given the ferrous sulphate treatment *after the hydrogen sulphide* treatment has converted the impurities to the sulphides (App. 15, 43 and 48).

(b) The Board of Appeals in its decision of September 28, 1948, (App. 107) held that the current efficiencies obtained according to applicants' method, as given in Table 3 of page 8 of the specification, are generally of the order of those obtained by Hannay. The evidence here shows that the current efficiencies obtained by Woodman and Royer are substantially higher than those obtained by Hannay (App. 44).

(c) The Patent Office Board of Appeals in its decision of September 28, 1948 (App. 107) held that the current efficiency of 63.06 for test 4 shown in Table 3 of the specification was due to the increase in voltage and current density and not to the method of purifying the solution, and that solutions 3 and 4 were identical. Woodman's testimony shows that these factual holdings are incorrect (App. 44 and 45).

(8) Alleged Departure Between the Theories Expressed in the Woodman and Royer Application and Those Expressed by Woodman at the Trial.

The opinion of the District Court states (App. 68) :

"The present position of the plaintiff as to the nature of the impurities remaining before that last step differs from the claims in the specification. In the specification the inventors state: '* * * we have been unable to identify even qualitatively the impurities removed in the iron purification or treatment step. Spectrographic analysis has failed to identify the impurities removed * * *. The tendency of metal sulphides to form colloids is well

known and free sulphur may be postulated as present in the solutions. It is possible that the function of the treatment step which we employ may be the removal of such solids, probably in the form of microscopic particles.' "

We shall show that:

(a) There is no departure between the *theories* expressed in the Woodman and Royer application and those expressed by Woodman at the trial; and

(b) If there were such departure as to *theory*, it would be immaterial.

(a) There is no departure. The District Court in its opinion has quoted a portion only of applicants' specification.

Applicants' specification on page 4 (App. 75) describes the process down through the step of adding a soluble sulphide such as ammonium sulphide or hydrogen sulphide to precipitate impurities such as iron, copper, nickel, cobalt, zinc and others. It then points out that the precipitated impurities are removed by suitable means such as by filtering the solution and that the resulting solution is "free of precipitated impurities." (App. 76)

The specification then states: (App. 76, 77)

"The final substantially pure solution resulting from the treatment by the above outlined series of steps is then treated by the addition thereto of a relatively small proportion, e.g. 2 g/l, of an iron compound, such as ferrous sulphate, the pH of the solution being regulated to be at least 4.5 or preferably above, and suitably between 7 and 8. On standing a relatively short time, a floc of iron compounds, preponderantly hydrates, is precipitated. This floc or precipitate appears to remove traces of harmful

impurities which are left in the solution after the usual purification procedure. We have not been able to establish the exact mechanism by which these impurities are removed, nor have we been able to identify even qualitatively the nature of the impurities. We have found repeatedly, however, and after a great number of experiments, that manganese sulphate electrolytes which refuse to yield a satisfactory manganese deposit prior to the treatment in accordance with our invention, would readily deposit manganese on the cathodes after the treatment step of our invention was employed.

"We have already pointed out that we have been unable to identify even qualitatively the impurities removed in the iron purification or treatment step. Spectrographic analysis has failed to identify the impurities removed. There are many instances referred to in the technical literature where solids have been absorbed by iron hydroxides and it appears that traces of impurities may be removed by this mechanism. *The purification, however, may be in part chemical.* The tendency of metal sulphides to form colloids is well known and free sulphur may be postulated as present in the solutions. It is possible that the function of the treatment step which we employ may be the removal of such solids, probably in the form of microscopic particles. Whatever the mechanism of purification may be, however, there is no question of the advantages of the treatment step in that solutions, from which manganese could not be deposited satisfactorily, were repeatedly made more susceptible to plating after the treatment."

The net effect of this whole disclosure as to the *theory* of how the invention works is that the applicants did not know why the process was successful, that it might be attributable to many things, but that they had found out by actual practice that they could take solutions which would not satisfactorily electrodeposit man-

ganese and by purifying them according to their process they would electrodeposit manganese satisfactorily. It is to be noted that the application states that the solution after treatment with hydrogen sulphide and filtering is "free of precipitated impurities." This is in agreement with Woodman's testimony at the trial. In referring to the chart (Plaintiff's Exhibit 2; App. 109), Woodman stated (App. 14) :

"The solution at Step (8) has been purified of some of the impurities. There still remains in solution, *not as suspended particles but actually in solution*, there still remains some impurities which, if allowed to go to the electrolytic cell, will cause what is known as re-solution of the manganese and the manganese will refuse to plate.

"Q. At that stage, the solution is clear also, isn't it, despite the fact that it contains these impurities?

"A. Yes. The solution from Step (8) goes through Filter (9) and in Filter (9) all suspended matter is removed. Therefore, the only things remaining in the solution are the impurities which are soluble and are in solution and therefore cannot be caught on filter (9)."

On cross-examination Woodman in referring to the solutions which had been treated with hydrogen sulphide said (App. 57) :

"We would take those solutions and many times filter those solutions through paper pulp an inch thick, try to plate them, filter them again through paper pulp an inch thick, which you know is one of the finest filtration aids that you can get, and still those solutions refused to plate, *which was certainly indicative that it was not suspended matter or colloids like that that was doing it*. It must have been some chemical compound in the solution that the filter could not touch.

"Now, we could take those solutions, treat them with our iron, filter, and the solutions would plate beautifully."

The statement in the District Court's opinion:

"The tendency of metal sulphides to form colloids is well known and free sulphur may be postulated as present in the solutions. It is possible that the function of the treatment step which we employ may be the removal of such solids, probably in the form of microscopic particles."

should be considered in connection with Finding of Fact No. 15 (App. 72) which reads:

"15. The applicants, at the time their specification was written, were of the opinion that the impurities remaining after the sulphide treatment were, possibly, in solution in the manganese solution. The specification states that after the sulphide treatment the solution is 'free of precipitated impurities.' "

When applicants' specification is considered as a whole it is evident that there is no departure between the theories expressed in the application and the theories expressed by Woodman at the trial.

(b) Even if there were a departure between the theories given in the application and those expressed by Woodman at the trial, it would be immaterial because it makes no difference whether the theory set forth in an application is wrong or whether any theory is expressed. It is merely necessary to disclose an operative process which one skilled in the art could follow and accomplish the desired results. There is no attack on the disclosure from this standpoint and there could not well be any such attack because the actual steps used in carrying

out applicants' process are clearly set forth in the specification.

Diamond Rubber Company of New York v. Consolidated Rubber Tire Company, 220 U.S. 428, 435-6, (U. S. Supreme Ct., 1911) :

"A patentee may be baldly empirical, seeing nothing beyond his experiments and the result; yet if he has added a new and valuable article to the world's utilities he is entitled to the rank and protection of an inventor. And how can it take from his merit that he may not know all of the forces which he has brought into operation? *It is certainly not necessary that he understand or be able to state the scientific principles underlying his invention, and it is immaterial whether he can stand a successful examination as to the speculative ideas involved.* Andrew v. Croos, 8 Fed. Rep. 269; Eames v. Andrews, 122 U.S. 40, 55; St. Louis Stamping Co. v. Quinby, 16 Off. Gaz. 135; Dixon Wood Co. v. Pfeifer, 55 Fed. Rep. 390; Cleveland Foundry Co. v. Detroit Vapor Stove Co. (C.C.A. Sixth Circuit), 131 Fed. Rep. 853; Van Epps v. United Box Co. (C.C.A. Second Circuit), 143 Fed. Rep. 869; Westmoreland Specialty Co. v. Hogan (C.C.A. Third Circuit), 167 Fed. Rep. 327. He must, indeed, make such disclosure and description of his invention that it may be put into practice. In this he must be clear. He must not put forth a puzzle for invention or experiment to solve but the description is sufficient if those skilled in the art can understand it. This satisfies the law, which only requires as a condition of its protection that the world be given something new and that the world be taught how to use it. It is no concern of the world whether the principle upon which the new construction acts be obvious or obscure, so that it inheres in the new construction."

Eames v. Andrews, 122 U.S. 40, 55, 56:

"It is to be observed that the scientific theory and principle, the application of which is supposed

to constitute the invention of Colonel Green, are not set forth either in the original or reissued patents. This feature was commented upon by Mr. Justice Blatchford in *Andrews v. Cross*, 19 Blatchford, 294, 305, as follows: 'It may be that the inventor did not know what the scientific principle was, or that, knowing it, he omitted, from accident or design, to set it forth. That does not vitiate the patent. He sets forth the process or mode of operation which ends in the result, and the means for working out the process or mode of operation. *The principle referred to is only the why and the wherefore. That is not required to be set forth.*'"

The Electric Storage Battery Company v. Shimadzu et al., 123 F. 2d 890, 897 (C.C.A. 3, 1941):

"An inventor is not required to know why his invention works, but if it does work he is entitled to the monopoly conferred by R. S. 4886 (35 U.S.C.A. 31)."

Shimadzu et al. v. Electric Storage Battery Company, 17 F. Supp. 42, 52 (D.C. E.D. Pa., 1936):

"The patent law is not concerned with abstract scientific principles, but with the means of usefully employing processes, apparatus, etc., which may result therefrom. As observed by Mr. Justice Holmes in *Minerals Separation Corporation v. Magma Company*, 280 U.S. 400, 403, * * * 'No one concerned in this business would care a straw as to the intimate nature of the action if it produced the result.'"

General Motors Corporation v. Swan Carburetor Company, (C.C.A. 6, 1937), 88 F. 2d 876, 886:

"It is not necessary that Swan understand all the scientific principles involved in his device [*A. O. Smith Corp. v. Lincoln Electric Co.*, 82 Fed. (2d) 226 (C.C.A. 6)]. It is only necessary that he make such disclosure and description of his invention that it may be put into practice. *Diamond Rubber Co. of New York v. Consolidated Rubber Tire Co.*, 220 U.S. 428, 436."

VI.

CONCLUSION.

The inventors made a meritorious invention not disclosed in the prior art. The judgment of the District Court dismissing the Complaint should be reversed. Plaintiff's prayer for an order finding that it is entitled according to law to receive a patent for this invention as set forth in the claim specified in Paragraph 6 of the Complaint should be granted.

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BRIEF FOR APPELLEE

United States Court of Appeals

DISTRICT OF COLUMBIA CIRCUIT

APPEAL NO. 10,928

VANADIUM CORPORATION OF AMERICA, APPELLANT

v.

JOHN A. MARZALL, COMMISSIONER OF PATENTS, APPELLEE

APPEAL FROM THE JUDGMENT OF THE UNITED STATES
DISTRICT COURT FOR THE DISTRICT OF COLUMBIA

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STATEMENT OF QUESTIONS PRESENTED

The appellee disagrees with the Statement of the Questions Presented which appears in the Brief for Appellant. In the opinion of the appellee, the question is whether the process set forth in the claims of the appellant's application involves an advance over the prior art amounting to invention and, thus, is entitled to patent protection under the provisions of R. S. 4886 (35 U.S.C. 31).

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*APPEAL FROM THE JUDGMENT OF THE UNITED STATES
DISTRICT COURT FOR THE DISTRICT OF COLUMBIA*

BRIEF FOR THE COMMISSIONER OF PATENTS

INTRODUCTION

This is an appeal from the judgment of the United States District Court for the District of Columbia (73)¹ dismissing the complaint (2-5) in an action under R. S. 4915 (U.S.C. Title 35, Section 63) in which the appellant, Vanadium Corporation of America, sought to have the court authorize the issuance of a patent on its application Serial No. 430,258 (74). The refusal of the patent by the Patent Office and the District Court was based upon lack of invention over the prior art.

¹ Unless otherwise indicated the numbers in parentheses refer to pages in the joint appendix.

APPELLANT'S APPLICATION

The application involved in this appeal relates to the preparation of manganese sulphate solution for electrolytic processing. Such preparation consists essentially of a series of purification treatments to eliminate undesirable chemicals from the manganese solution. For the purposes of this appeal it is necessary to consider only the final few steps which, in the prior art, as exemplified by the Hannay et al. patent No. 2,259,418 (141) and the Bureau of Mines Report No. 3406 (111), comprised (1) treating the solution to remove such impurities as iron and arsenic and (2) converting certain other metal sulphate impurities (e.g., nickel, copper) to sulphide precipitates by the use of hydrogen sulphide.

According to the appellant's application certain residual impurities remained which inhibited proper plating in the electrolytic phase of the process.

The appellant's alleged invention is directed toward the elimination of these residual impurities and, to that end a soluble metal salt, such as iron sulphate, is added to the solution which, according to the specification, has the desired effect of removing the impurities and rendering the electrolysis uniformly effective.

In summation, the appellant bases its claim of invention on adding to the prior art processes an allegedly new purification step to remove residual impurities.

THE HANNAY ET AL. PATENT

The Hannay et al. patent No. 2,259,418 (141) was cited merely to show the conventionality of the preliminary treatment, including the use of hydrogen sul-

phide, as set forth in the first full paragraph on page 144 of the joint appendix, as follows:

“While we do not wish to limit the scope of our present invention to any particular purification step, we have found that the use of hydrogen sulphide for the precipitation of metallic impurities present in solutions containing manganese is particularly suitable in this step of the process, after removal of iron by standard methods.”

THE BUREAU OF MINES R. OF I. NO. 3406

The Bureau of Mines R. of I. No. 3406 (111) was cited to show, and was held by the District Court to constitute, a teaching of the crucial step in the appellant's process, the addition of a soluble metal salt. As was developed at the trial (51), the reference admittedly suggests the use of iron sulphate as an addition agent for manganese sulphate solutions for the express purpose of precipitating the arsenic impurity. The reference does not specifically set forth that this treatment should follow the soluble sulphide purification step, the sequence specified in the claims.

THE PRESCOTT AND JOHNSON PUBLICATION

Pages 114, and 115 of “Qualitative Chemical Analysis”, 5th Edition (151, 152) set forth, in the last paragraph on page 114, ending at the top page 115, that treatment of a solution to precipitate arsenic by the use of hydrogen sulphide will not completely eliminate the arsenic if much pentad arsenic is present in the solution. The reference thus establishes that a solution which has been treated with hydrogen sulphide might well contain arsenic unless it is known with certainty that no arsenic in the pentavalent form was present.

SUMMARY OF ARGUMENT

1. The issue presented for decision is whether the District Court was clearly wrong in agreeing with the Patent Office that the appellant's contribution was no more than a routine step forward in the art, not amounting to invention.

2. The appellant's application disclosed that it was reasonable to suspect that the impurities were colloidal in nature and that it was well known that colloids could be removed by treatment with soluble metal salts, such as iron sulphate.

3. The applicants' contribution was obvious in view of the state of the art as disclosed in the specification of the application.

4. In view of evidence introduced at the trial it was reasonable to suspect that traces of arsenic were present in the electrolyte following the H_2S treatment.

5. Since the Bureau of Mines Report No. 3406 taught that arsenic could be removed by the use of ferrous sulphate, the addition of this step to the prior art treatment was obvious.

6. The record fails to show that the applicants solved a long standing problem that others, skilled in the art, tried to solve and failed.

7. The appellant's contention that a single reference must show the total combination to negative patentability is without basis in the law.

ARGUMENT

After a careful and impartial study of all the evidence in the case, the District Court found (67-69) that it was in complete accord with the Patent Office holding, that, in view of facts within the knowledge of the applicants, including the prior art teachings, the step

forward outlined in the appealed claims was one which should have been obvious to a skilled worker in that art. Accordingly, it properly held that the results attained were no more than the result of routine experimentation, representing merely a step forward in the gradual development of an art.

Assuming that the facts accord with this premise, it is well settled law that even though a process be both novel and useful, if it is the result of routine experimentation, it is lacking in invention and, thus, unpatentable. In *Mandel Bros. Inc. v. Wallace*, 335 U. S. 291, 79 U.S.P.Q. 220, it is stated:

“But we think that the state of the prior art was plainly sufficient to demonstrate to any skilled chemist searching for an anticorrosive agent that he should make the simple experiment that was made here. * * * Skillful experiments in a laboratory, in cases where the principles of the investigation are well known and the achievement of the desired end requires routine work rather than imagination do not involve invention. * * * The step taken by the patentees in advance of past knowledge was too short to amount to invention.”

Holdings of the same import are to be found in *Minnesota Mining and Mfg. Co. v. Coe*, 69 App. D.C. 219, 99 F. 2d 986 and *Standard Oil v. Marzall*, 86 U. S. App. D.C. 210, 181 F. 2d 280.

In this appeal, therefore, the Court is called upon to decide the following single issue:

Does the record in the case show that the District Court and the Patent Office were clearly wrong in holding that the appellant's advance over the

prior art was a routine step forward in the art, not amounting to invention?

It is submitted that the evidence in the case falls far short of showing clear error and, indeed, shows without question that the appellant's process lacks invention.

THE APPLICANTS' CONTRIBUTION WAS OBVIOUS IN VIEW OF THE
STATE OF THE ART AS DISCLOSED IN THEIR SPECIFICATION

In order to correctly determine the question of obviousness in any case involving this issue, the first logical step is to examine the storehouse of knowledge upon which the experimenters could draw prior to the discovery.

According to the specification in the application, it is disclosed on page 75 of the Joint Appendix, lines 4 to 8, that it was known that small traces of impurities would inhibit manganese deposition. Thus, it was known that the failure of prior art processes was due to impurities in the final manganese sulphate bath, which were not removed by the known procedures.

Moreover, the specification states (77, lines 7 to 11)

"The tendency of metal sulphides to form colloids is well known and free sulphur may be postulated as present in the solutions. It is possible that the function of the treatment step which we employ may be the removal of such solids, probably in the form of microscopic solids."

To state it another way, the applicants knew that metal sulphides, such as the nickel and copper sulphides resulting from the H_2S treatment step, tended to form colloids which would pass through the filter and remain in the solution as impurities. It is stated that this

tendency was "well known" and, thus, the possibility, or even probability, of colloidal impurities would be readily apparent to a skilled worker, even without the need for experiments.

It is proper, at this point, to determine what action the ordinary skilled experimenter could be expected to take, without exhibiting unusual talent, to eliminate the impurities. In view of what was known, or suspected, of the nature of the impurities (as being colloids), any of the recognized methods for precipitating or otherwise removing colloids must necessarily be considered obvious possibilities for trial. If the known methods were tried and found ineffective, the development of a new purification step may be said to involve unusual talent amounting to invention.

If, on the other hand, the problem was solved by merely using a recognized solids removing purifying step, the advance in the art was routine and, under the rule, not deserving of patent protection.

Referring to the particular facts here, therefore, if the iron sulphate treatment constituted a known means for removing small traces of solid impurities, the appellant's process cannot be said to be inventive. The specification of the application supplies this crucial information as follows (77, lines 2 to 6) :

There are many instances referred to in the technical literature where solids have been absorbed by iron hydroxides and it appears that traces of impurities may be removed by this mechanism.

Thus, the use of iron salts to form hydroxides to carry down solids to purify solutions was a known and recog-

nized purification treatment. The record is completely devoid of any showing that the result of using this step in purifying manganese sulphate would be unpredictable nor is there any contention that the coaction of this step with the other steps of the process brings about an unobvious result.

The only conclusion, therefore, is that, on the basis of the application disclosure alone, the applicants' advance was merely a routine step forward in the development of the art, and that it was unnecessary for them to contribute the uncommon talent required for invention in order to reach the desired result.

THE ADDITION OF THE IRON SULPHATE STEP SHOULD HAVE BEEN OBVIOUS IN VIEW OF THE BUREAU OF MINES REPORT NO. 3406

Additional evidence of the obviousness of the applicants' contribution is found in the Bureau of Mines Report of Investigation No. 3406 (111). On pages 7 and 8 of the Report (115, 116) there appears, under the title "Impurities in Manganese Electrolyte" a discussion of a number of different types of impurities, with suggestions of treatments to effect their removal. Under the sub-title "Arsenic", the Report suggests, in connection with the removal of arsenic:

"Accordingly, ferrous iron in the form of metallic iron or ferrous sulphate was added to the impure leach solution when the ferrous-iron content was less than 0.1 gm per liter."

The import of this reference, therefore, is that an iron sulphate treatment was known to be effective in removing arsenic from manganese sulphate electrolyte. Although the diagrams in other portions of the Report

indicate that such treatment usually preceded the conversion of the nickel and copper to sulphides, there is no suggestion that the iron sulphate step would not be equally effective in removing traces of arsenic following a sulphide treatment.

Hence, this ground of rejection depends upon whether skilled workers in the art could have been reasonably expected to suspect the presence of traces of arsenic in the electrolyte following the H_2S purifying step, and certain evidence introduced at the trial tending to establish this fact may be summarized as follows:

1. As set forth above, the Prescott and Johnson Test (151, 152) states unequivocally that an H_2S treatment will not remove all arsenic if too much is present in the pentavalent state.

2. Plaintiff's exhibits 6, 7 and 8 state that an iron sulphate treatment following an H_2S step (appellant's process) will remove traces of arsenic. Thus, the plaintiff's own exhibits demonstrate that all arsenic is not removed by the sulphide step, and one of the purposes of their process is the removal of traces of arsenic (131, second column, lines 21 to 26; 138, lines 19 and 20; 140, lines 35 and 36).

3. One of the applicants, in testifying at the trial, admitted that arsenic could well "slip through" the sulphide treatment (54)

The evidence shows conclusively therefore, that experimenters should have predicted the presence of arsenic traces in the electrolyte prior to the appellant's final step. Although the exact nature of the impurities causing the trouble was unknown (76, first full paragraph) the applicant had every reason to suspect traces of arsenic. In view of the Bureau of Mines sug-

gestion for removing arsenic, the addition of iron sulphate becomes an obvious possibility for overcoming the trouble and an expedient which should have occurred to experimenters in the art without the need for exhibiting any unusual talent.

THERE IS NO EVIDENCE THAT APPLICANTS SOLVED A LONG STANDING
PROBLEM WHERE OTHERS HAVE FAILED

The statement on page 27 of the appellant's brief (3rd paragraph) that others have long attempted to meet the problem without success is not supported by the record. The testimony in the case (as summarized on pages 21 to 24 of Appellant's Brief) brought out merely that the numerous other persons mentioned were either associated with the applicants and were familiar with the problem or acted in a supervisory capacity over the applicants. There is no evidence that any persons, other than the applicants themselves, actively engaged in the experimental work. Accordingly, the record falls far short of showing that others tried and failed, where the applicants succeeded. This case is distinguished from the *Kelley v. Coe* case cited by the appellant (App. Brief 24) on this point alone. In that case, the court states, "But although a number of experimenters attempted to achieve the desired result, the important fact is that none of them succeeded." The mere failure of others to come forward with a solution for the problem does not make the solution any less obvious. *Paramount Publix Corp. v. American Tri-ergon Corp.*, 294 U.S. 464.

IT IS NOT NECESSARY THAT ONE REFERENCE SHOW THE ENTIRE
COMBINATION TO ESTABLISH LACK OF INVENTION

On page 29 of the appellant's brief, it is contended that the rejection of the appealed claims is not proper

since no one reference shows the combination of a soluble sulphide treatment followed by the addition of ferrous sulphate. However, a study of the authorities will show a number of decisions specifically holding that a single reference showing the general combination is not necessary to negative patentability. For example, it was stated in *Gilbert et al. v. Marzall*, 85 USPQ 288, 637 O. G. 981, that:

It is, however, well established that "Where a patent includes a combination of elements, it is not necessary to establish anticipation that all of the elements be found in a single earlier patent or in a single device previously in general use. It is enough if the evidence, taken as a whole, discloses that all of the claimed elements are found in different prior patents in the art or in different devices previously in general use, and no new functional relationship arises from their combination."

Similar holdings are found in *Radke v. Coe*, 74 App. D. C. 251, 122 F. 2d 937, *In re Goepfrich*, 30 CCPA 1181, 136 F. 2d 918 and specifically in connection with processes in *In re Mulholland*, 37 CCPA 983, 181 F. 2d 249. The correct rule, which is apparent from these decisions and others, is that where the references in the prior art show individual features of the claims, there is no invention where the act of combining those features should have been obvious. This conforms to the facts in this case as hereinbefore set forth.

CONCLUSION

For the reasons given, it is submitted that the applicant's contribution to the art involved nothing more than adding a known purifying step at the end of the

prior art purifying process. Moreover, the step was one which should have been obvious to the applicants in view of their postulation of the presence of colloids and, further, in view of the Bureau of Mines Report No. 3406. The record does not establish that the applicants exhibited the "uncommon talent" and "creative genius" required by the doctrine announced in *Standard Oil v. Marzall*, 86 U. S. App. D. C. 210, 181 F. 2d 280, but rather that the facts show "an example of the natural step by step development of the art" as referred to in *Sinclair Refining Co. v. Coe*, 78 U. S. App. D. C. 176, 138 F. 2d 673.

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